TEXTILE RESEARCH JOURNAL

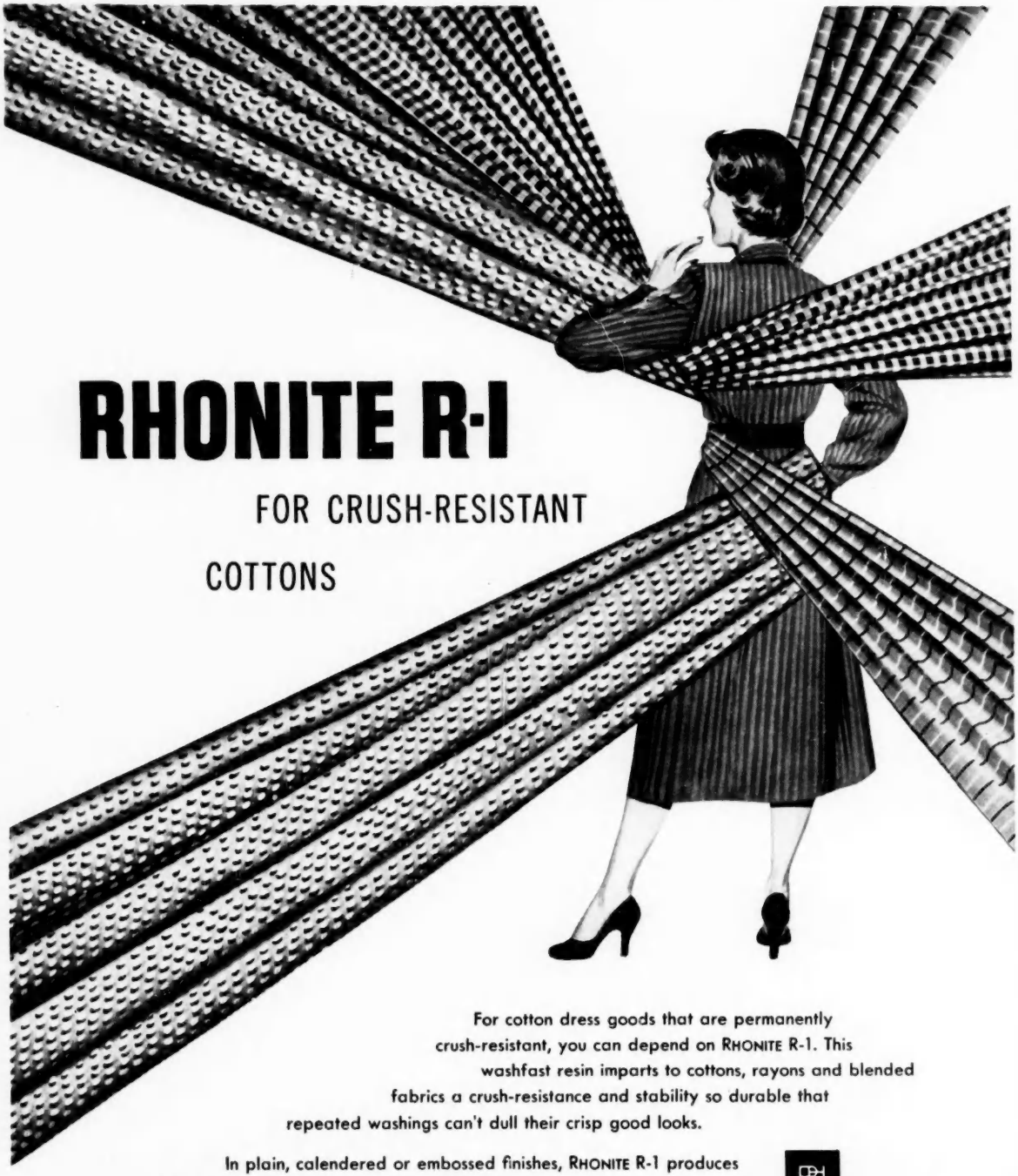
VOLUME XXIII December, 1953 NUMBER 12

Annual Index Issue

PUBLICATION OF

TEXTILE RESEARCH INSTITUTE

Editorial Office: 10 East 40th Street, New York 16, N. Y.



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VOL. XXIII, No. 12 December, 1953

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TEXTILE RESEARCH JOURNAL, published monthly at Prince and Lemon Streets, Lancaster, Pa., is devoted to the interest of research in textile and allied industries. It is published by Textile Research Institute.

Manuscripts and communications should be sent to the editorial office, 10 East 40th Street, New York 16, N. Y.

Subscription rates:
$15.00 per year; additional for postage, 50 cents to Canada, $1.00 to all other countries. Single copies, $1.50 each.

Entered as second-class matter, April 27, 1945, at the post office at Lancaster, Pa., under the Act of August 24, 1912. Accepted for mailing at special rate of postage provided for in paragraph (d-2), Section 34.40, P. L. & R. of 1948, authorized May 9, 1950.

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TEXTILE RESEARCH JOURNAL

VOL. XXIII, No. 12 DECEMBER, 1953

Starch Studies

Part IV. Concepts of Structure*

Albert W. Bauer† and Eugene Pacsu‡

Contribution from Textile Research Institute and Frick Chemical Laboratory, Princeton University, Princeton, New Jersey

Introduction

Efforts to determine the structure of the starch granule have resulted in an increasing number of theories without the resolution of those previously proposed. It is generally conceded, however, that starch may be fractionated into two main components: amylose, an essentially straight-chain polyglucoside, and amylopectin, a branched-chain polyglucoside. The object of this investigation is to determine how these two materials are assembled to form the starch granule.

Using peptizing agents or heating will swell starch granules in water. A significant observation is that whereas reagents such as sodium iodide, urea, and sodium thiocyanate will apparently swell the granules to spheres of limiting size [14], prolonged heating in water results in the dispersion of the starch [28]. Although cold, strong caustic has been generally accepted as a solvent for starch, it has recently been demonstrated, with the aid of the phase microscope [2], that large particles may be observed in starch that has been dispersed in *normal* potassium hydroxide for 2½ hrs.

In nearly all varieties of starch, amylose is the minor component, constituting about 25% of corn, potato, and wheat starches. Glucose anhydride units are joined together by 1,4-α-glucopyranosidic bonds [17] to form straight chains having an average molecular weight of about 50,000 [19, 21, 23, 36]. It is believed that the polymer is coiled into a long helix [12, 15] which makes one complete turn every six glucose units. However, recent investigations [22, 32, 33, 34] have indicated that amylose is not entirely devoid of branching. Amylose absorbs numerous materials, such as lower-molecular-weight aliphatic alcohols, thymol, borneol, cyclohexanol, nitroparaffins, fatty acids, and iodine, the last imparting an intensely blue color to the complex. A sample of purified amylose will absorb approximately 20% of its weight of iodine, forming a tightly bound complex. It has been proposed that the various complexing reagents are absorbed into the hollow tube formed by the helical polymer [37, 38]. The stabilities of the resulting complexes however, vary from one reagent to another.

The other main carbohydrate constituent of starch is amylopectin, which unlike amylose is completely soluble in water. Basically, the structure of amylopectin, like that of amylose, is the linear 1,4-α-anhydroglucopyranoside; however, amylopectin chains

* Parts IV–VII are based on a thesis submitted by Albert W. Bauer in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Princeton University.

Parts I and II appeared, respectively, in the July and October, 1942, issues of *Industrial and Engineering Chemistry*; Part III in the March, 1943, issue. Parts V–VII follow in this issue.

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possess branches [10, 11, 16, 18, 26] which originate at the carbon 6 (primary) hydroxyl groups of approximately 3%–5% of the glucose anhydride units. Molecular weight determinations of amylopectins have yielded values ranging from 100,000 [21] to 420,000,000 [44] for the acetate, the great differences being largely due to the incompatibilities of the methods of measurement.

Whereas amylose will absorb about 20% iodine by weight, amylopectin absorbs less than 1% iodine, exhibiting a red-purple color. Furthermore, amylopectin does not form complexes with aliphatic alcohols, nitroparaffins, etc. This difference in the absorption properties of the two fractions not only furnishes a method for their separation, but also provides the bases for several methods of quantitatively differentiating between amylose and amylopectin in a mixture of the two. Thus, a starch sample which absorbs 10% of its weight of iodine is composed of 50% amylose and 50% amylopectin.

The facility of amylose to complex with many polar organic compounds has led to an efficient method of starch fractionation [3, 39, 40, 41]. Fatty acids, nitrobenzene, and lower-molecular-weight alcohols are just a few of such reagents. A typical separation [25, 40] is carried out by dispersing a starch sample in water by autoclaving or boiling the mixture. The polar reagent may be added to the aqueous solution before or after the starch has been dispersed. As the solution cools, a complex of amylose and the polar organic reagent will precipitate from the solution. Excellent separations have been achieved using butanol or Pentasol (a commercial mixture of amyl alcohols).

Bourne, Donnison, Haworth, and Peat [4] studied the efficiency of the separation of amylose and amylopectin from starch pastes using thymol at various pH's. They concluded that there were no significant differences in the yields or in the Blue Values of the amyloses obtained within the range of pH 5 to pH 11. Potato starch was fractionated using cyclohexanol as a complexing agent. The resulting amylopectin fractions were of higher purity than those obtained from the butanol and Pentasol methods. The amylose, however, was found to be of lower purity than that obtained with the aforementioned alcohols, due to the presence of coprecipitated amylopectin.

The Chemical Structure of the Starch Granule

Starch chemists at present remain divided into two schools of thought—one group subscribing to the multiple concept of starch structure, and the other advocating the unitary theory. Briefly stated, the former concept is that amylose and amylopectin exist in the native starch granule as separate chemical compounds; the unitary theory is that amylose and amylopectin are joined together by covalent bonds which are broken when the two polysaccharides are separated. Many variations of the unitary concept exist, ranging from the contention that one amylose molecule is bonded to one amylopectin molecule to form a starch molecule, to the suggestion that each starch granule is one large molecule, the apparent components being welded together by covalent links.

The Multiple Concept

Based on the multiple concept, numerous variations of the arrangement of the molecules in the granule are possible. Probably the most widely accepted structure represents the granule as consisting of a shell of amylopectin that surrounds amylose, the component of the granule core [13, 28]. Thus, if the granule were ruptured, amylose would be released, leaving an empty sack composed of amylopectin.

Another possible arrangement of the components is one in which the amylose and the amylopectin form a solid solution, the molecules being mixed randomly. In this case, a considerable amount of hydrogen-bonding between the amylose and the amylopectin is possible. It has also been suggested that the complex interentanglement of the molecules may be a major force in preserving the granule structure [21], and that drastic heating is needed to disentangle the chains and permit fractionation. Both hydrogen-bonding and molecular entanglement could, of course, provide stability to the granules in either model, if the amylose and the amylopectin were in separate parts of the granule or if they formed a solid solution.

Nearly all of these proposals involve a single basic chemical structure [17] of each of the components—amylose (a 1,4-α-polyanhydroglucopyranoside), and amylopectin (a similar polymer containing 1,6-α-branching every 20 to 30 monomer units). Although this structure has received popular support, not all investigators have accepted the polypyranoid formulation. Since detailed discussions of the mul-

tiple concept are available in well-known textbooks on starch [21, 43], it does not seem necessary to review here the extensive literature on the subject.

The Unitary Concept

In general, proponents of the unitary concept believe that amylose and amylopectin are artifacts resulting from a chemical hydrolysis of the starch molecule.

Furanoid-Pyranoid Structure

As a direct result of his investigations of the change in optical rotation of starch solutions in enzymic hydrolysis, Kuhn [24] proposed that starch molecules consist of alternating glucofuranoid and glucopyranoid rings.

Blom and Schwarz [3] recently hydrolyzed starch by several methods, and followed the change in the optical rotation of the solution as a function of the reducing power of the starch solution. They proposed that if every hydrolyzed bond in starch is a 1,4-α-glucopyranosidic bond (the effect of the few 1,6-α-glucopyranosidic bonds is considered negligible), then the change in rotation of the solution due to the splitting of one 1,4-α-glucopyranosidic starch bond is the same as that due to the hydrolysis of one maltose molecule to form two glucose molecules.

The investigators hydrolyzed starch with acid, α-amylase, and β-amylase, and followed the change in optical rotation of the solution coincident with the increase in the reducing power of the solution. They discovered, however, that the change in optical rotation of the starch solution per millimole of hydrolyzed glucosidic bonds ($[Sp]_D$) was not a constant value, but that it increased during the hydrolysis, approaching a final value which corresponded to the change in rotation resulting from the hydrolysis of one millimole of maltose into two millimoles of glucose.

Blom and Schwarz interpreted these data as indicating that starch possesses some type of link which is more readily hydrolyzable than are the 1,4- and 1,6-α-glucopyranosidic bonds. They proposed a starch model which consists of chains of alternating glucopyranose and glucofuranose residues (Figure 1). Whereas acid hydrolysis attacks both types of links, the 1,5-bonds are hydrolyzed more readily than the 1,4-links, as evidenced by the fact that $[Sp]_D$ values during the acid hydrolysis of starch increased continuously until, after about 90% hydrolysis, the $[Sp]_D$ of the solution approximated that of the hydrolysis of maltose to form glucose. The $[Sp]_D$ value seemed to remain constant (over the short range that was measured) during β-amylase hydrolysis of starch, and was smaller than that obtained from the hydrolysis of maltose. The authors suggested that β-amylase hydrolyzes 1,5-links, leaving the 1,4-bonds intact. In support of this contention, they pointed out that the $[Sp]_D$ values of the hydrolysis of known furanosides are smaller than those of corresponding pyranosides.

Glucosidic Bonds of Unknown Nature

Swelling and gelatinization are known to be endothermic processes [27, 29], just as is dextrinization. Bawn, Hirst, and Young [1], quantitatively studying the reaction velocity and activation energy of the disaggregation process of methylated starch, noted that ". . . the initial action of acid upon the methylated starch is very rapid, and not until a molecular weight of about 200,000 is reached does the first order equation become valid." Since the second stage of the reaction (from 200,000 to 20,000 molecular weight) appeared to be a hydrolysis of the first order, they measured the activation energy of this process, obtaining a value of 20.7 kcal.* Inulin, a 1,2-polyanhydrofructofuranoside, was also methylated and hydrolyzed in order to establish a basis for comparison. The rate of the hydrolysis of the methylated inulin was some six times greater than that of the disaggregation of the methylated starch, and the activation energy was found to be 25.5 kcal. Nevertheless, the rates of the hydrolysis of both of these materials are greater than that of the 1,4-α-anhydroglucopyranosidic bonds of methylated starch. Bawn and coworkers then concluded that because the activation energy of the secondary stage of the disaggregation of methylated starch is intermediate between the activation energy of the hydrolysis of a

* Recalculation of these authors' data gave 18.9 kcal.

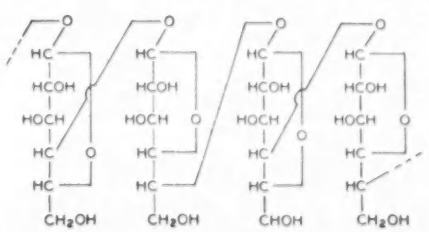

FIG. 1. *Furanoid-pyranoid structure of starch, according to Blom and Schwarz.*

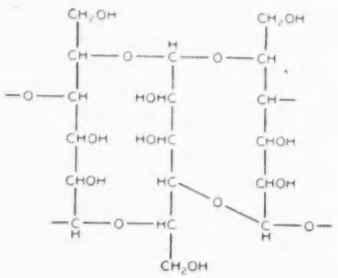

FIG. 2. *Open-chain acetal structure of starch, according to Pictet.*

polyfuranoside and that of a polypyranoside, this stage of the disaggregation process must involve the breaking of covalent bonds.

Isolation of the hydrolysis products of highly methylated starch, however, has provided no evidence for the presence of glucopyranosidic bonding on carbons 2 or 3. The 1,6-bonds in starch are generally known to be more resistant to acid hydrolysis than the 1,4-linkages.

Open-Chain Hemiacetal and Acetal Bonds

The Pictet theory.—Pictet [35], in 1930 proposed an open-chain acetal structure for starch (Figure 2). According to this structure, each anhydroglucose unit is bound to the preceding and

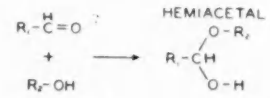

FIG. 3. *Hemiacetal bond.*

succeeding ones through carbons 1, 4, and 5; the carbon 1 of each unit is linked to two other anhydroglucoses, one bond being α and the other β. Methylation treatment would replace the hydroxyl groups at carbons 2, 3, and 6 with methoxyl groups, as they would be substituted in a 1,4-α-polyanhydroglucopyranoside. Acid hydrolysis of Pictet's model might cleave either the 1,4- or the 1,5-bonds, and would exhibit no selectivity for either α- or β-bonds. Four types of linkages would therefore exist in the natural starch and in degradation products: 1,4-α-, 1,4-β-, 1,5-α-, and 1,5-β-anhydroglucose bonds. Although neither chemical nor enzymic degradation has substantiated the presence of 1,4-β-, 1,5-α-, and 1,5-β-bonds in starch, Pictet's hypothesis does make a definite contribution to the theories of starch structure. First and most important is the concept of the open-chain acetal, which, he pointed out, would be acid-sensitive. Secondly, Pictet demonstrated that the methylation technique does not provide a unique answer to the structure of polysaccharides. Models such as his would yield methyl

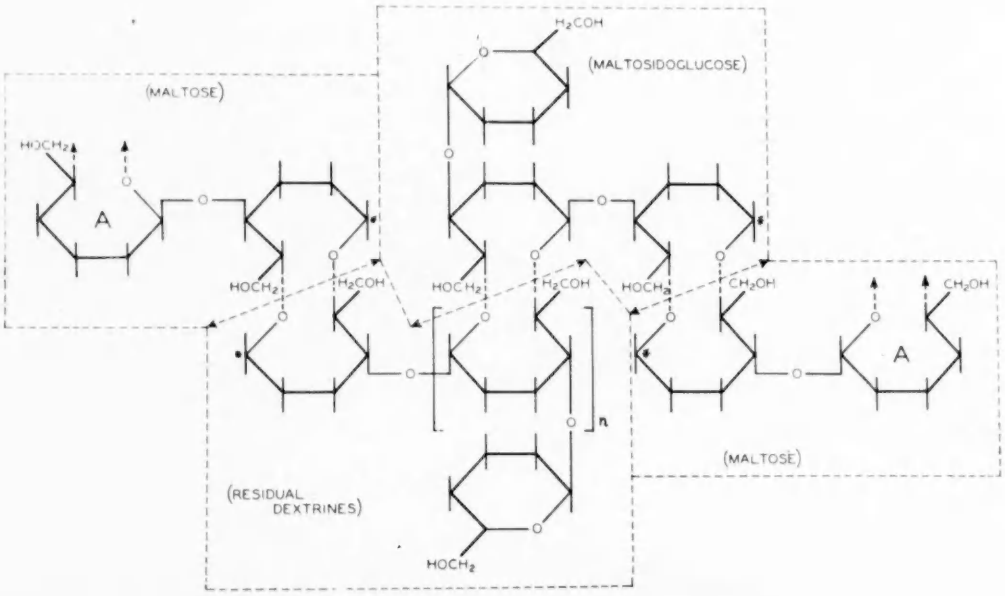

FIG. 4. *Dumazert open-chain starch structure.*

derivatives identical to those produced from the linear glycopyranosides.

The Pacsu theory.—In 1946, Pacsu and Hiller [31] proposed that starch polymer chains are cross-linked with glucosidic links at the reducing end-groups. They pointed out that each of the reducing ends of the chains in their model possesses one hydroxyl group on carbon 1, which forms part of the cross-link. This type of grouping may be recognized as a hemiacetal unit (Figure 3). Although such compounds are stable in the presence of strong alkali, they are readily hydrolyzed by weak acids to yield an alcohol and an aldehyde. Acid hydrolysis of the Pacsu-Hiller starch model would dissect the chains from one another at the reducing ends.

This structure has since been modified by Pacsu [30]. Again, cross-links at the reducing ends of the polymer chains would produce hemiacetal groups; however, the modified structure permits the cross-links to occur at any position along the chain, forming acetal groups. Pacsu suggested that one should expect both the acetal and the hemiacetal structures to be acid-sensitive, acid hydrolysis cleaving these links at a far greater rate than it splits the normal glucosidic bonds. Thus, the starch molecule would rapidly be hydrolyzed into amylose and amylopectin, further hydrolysis resulting only in the degradation of the polymers.

The Dumazert theory.—The acetal cross-link plays a fundamental role in the starch model (Figure 4) proposed by Dumazert [7]. Calling attention to the fact that elemental analyses of starch [6] indicate a carbon content of 42.3%, whereas the theoretical value is 44.4% for the formula $(C_6H_{10}O_5)_n$, he suggested that the basic unit of starch is not anhydroglucopyranose, but $(C_{12}H_{22}O_{11})_n$ (Figure 5), the elemental carbon analysis of such a polysaccharide being 42.1%.

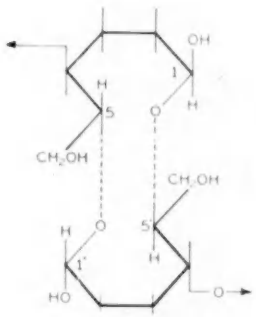

FIG. 5. *Dumazert monomer in starch.*

Further evidence was obtained from the acid hydrolysis of starch [6]. Complete hydrolysis of a simple polyanhydropyranoside would proceed according to the formula:

$$(C_6H_{10}O_5)_n + nH_2O \rightarrow nC_6H_{12}O_6.$$

Calculating the quantity of starch that must be hydrolyzed in order to obtain 1 g. of glucose, Dumazert divided the molecular weight of one anhydroglucose unit (162) by the molecular weight of glucose (180) to obtain the value of 0.900. Thus, x grams of glucose should result from the hydrolysis of $(162/180)\ x = 0.900\ x$ g. of starch. However, by carefully hydrolyzing samples of starch in acid, Dumazert demonstrated that 1.00 g. of glucose re-

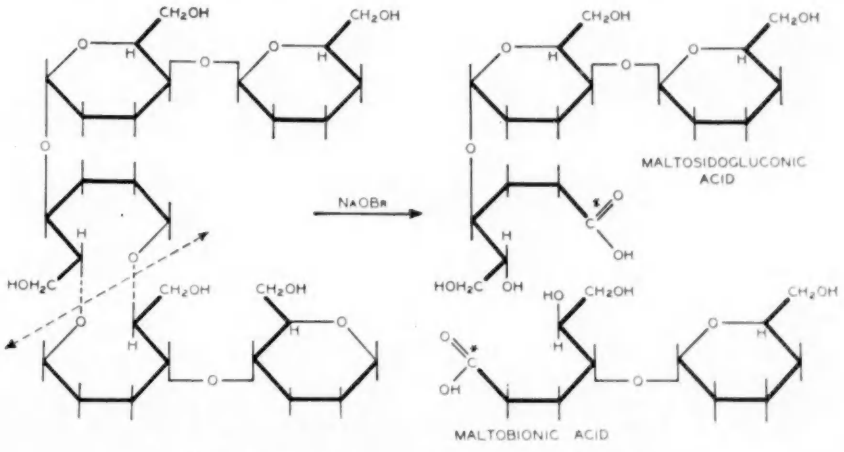

FIG. 6. *Dumazert oxydolysis reaction of starch.*

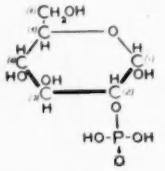

FIG. 7. *Phosphate ester (glucose-2-phosphate).*

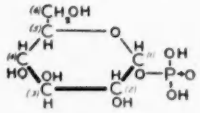

FIG. 8. *Phosphatide (glucose-1-phosphate).*

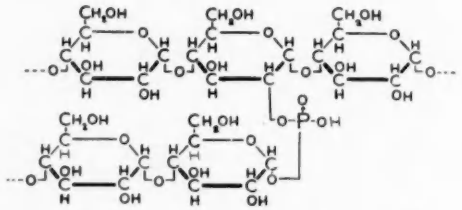

FIG. 9. *Starch phosphate cross-link, according to Sutra.*

sults from the hydrolysis of 0.945 g. of starch, and not from the theoretical quantity of 0.900 g. If the basic unit of starch were $(C_{12}H_{22}O_{11})$, then the hydrolysis equation would be

$$(C_{12}H_{22}O_{11})_n + nH_2O \rightarrow 2n(C_6H_{12}O_6).$$

Dividing the molecular weight of the monomer unit (342) by twice the molecular weight of glucose (360), Dumazert obtained a new factor of 0.950. As the value of 0.950 is in much closer agreement with the experimentally determined 0.945 than is 0.900 (the factor corresponding to a polyanhydroglucopyranoside), Dumazert concluded that the $(C_{12}H_{22}O_{11})_n$ formula is more likely to represent the structure of starch than is the polyanhydroglucopyranoside structure.

Three types of degradation are possible according to Dumazert. Like the Pacsu model, Dumazert's starch is cleaved at the acetal links by mild acid hydrolysis (dotted lines in Figure 4); however, a variety of products from this treatment might be expected. Possible artifacts are amylose, amylopectin, dextrins, maltotriose, and maltose, depending upon the extent of the hydrolysis. Strong acid hydrolysis will, in addition to breaking the acetal links, rupture the normal glucosidic bonds, ultimately degrading the polymer to glucose.

When the starch is oxidized by sodium hypobromite, a third type of cleavage occurs, "oxidolysis," as shown in Figure 6 [7, 8, 9]. Dumazert claims to have isolated both maltobionic acid and maltotrionic acid as the main products of this reaction. As indicated by dotted lines (Figure 6), oxidolysis will cleave the acetal links, oxidizing the reducing end-groups to carboxyls (marked with asterisks in Figure 6).

Phosphate Cross-links

It is generally known that all the common starches contain bound phosphate groups. The bound phosphoric acid forms esters predominantly with either the amylose or the amylopectin fraction. While nearly all of the phosphorus of potato starch (about 0.2% based on P_2O_5) is found in the amylopectin component, that of wheat starch (about 0.2% based on P_2O_5) is in the amylose component. Like typical ester bonds, the links binding phosphates to carbon 2, 3, 4, or 6 positions (Figure 7) are fairly stable in acid medium, but may be hydrolyzed by alkali. On the other hand, if the phosphate is linked to the reducing end of a chain forming a phosphatide bond, the structure is of the glycoside type. Glucose-1-phosphate (Figure 8), for example, is not readily hydrolyzed by refluxing in caustic solution; however, warming the compound in dilute acid or refluxing in water will rapidly remove the phosphate group.

If, then, amylose chains were bonded to the esterified phosphate groups of the amylopectin fraction (as might be true in the case of potato starch) through phosphatide links [42] at the reducing ends of the amylose chains (Figure 9), acid hydrolysis would rupture the phosphatide bonds, releasing amylose and amylopectin chains, the latter containing the esterified phosphate groups. In the case of wheat starch, the phosphate groups would be bound to the amylose chains through ester bonds and bound to the reducing ends of the amylopectin chains through phosphatide bonds. Prolonged refluxing in water would cause the same cleavage. These two treatments are the same as those commonly used to disaggregate granular starch in the gelatinization stage, preceding fractionation.

Indeed, the presence of a phosphatide bond is not a matter of mere surmise. That glucose-1-phosphate is an intermediate compound in the biological synthesis of potato starch [5] has been well established, so that the presence of such a group in the final product might be expected.

The true structure of natural starch is not necessarily described by any one of the preceding theories. Higginbotham and Morrison [20] attempted to obtain pure amylose and pure amylopectin from a sample of starch in 100% yield. They discovered, however, that generally not more than 80% of the material could be fractionated, some 20% remaining securely associated. These results seem to indicate that the forces that hold 80% of the starch together in the granule are weaker than those which bind the remaining 20%.

Conclusion

Chemical or analytical methods available for structural studies of starch are not suitable to prove or disprove the validity of either the multiple or the unitary concept of starch structure. However, the independent existence of constituents of at least two main types of structures, linear and branched, in *any* starch solution is to be expected on the basis of the multiple concept. In contrast, the unitary theory postulates that native starches exist as uniform materials in neutral or alkaline dispersions and, consequently, no fractionation can possibly take place when such dispersions are employed as starting materials. Our experimental results, which led to two improved methods of starch fractionation (to be discussed in Part V), are difficult to interpret on the basis of the multiple concept, but are readily understood from the view of the unitary theory of starch structure.

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(*Manuscript received August 11, 1953.*)

Starch Studies

Part V. Alkali and Acid Processes of Starch Fractionation

Albert W. Bauer and Eugene Pacsu

Introduction

In the preceding paper (Part IV) it was concluded that fractionation of native starch dispersed in an alkaline medium could not possibly take place if the linear and branched constituents were held together by acid-sensitive but alkali-resistant covalent bonds as postulated by the unitary theory. On the other hand, fractionation could be readily attained provided that such linkages were first ruptured by the powerful catalytic action of hydroxonium ions. Clearly, the formation or nonformation of fractions from an alkaline dispersion of native starch might then be used as evidence in favor of one or the other of the two opposing theories.

The first method, named "alkali process," is based on the discovery that solutions of native starch prepared with alkali can be readily fractionated provided that the solutions are first neutralized and then heated above 60°C for a short time. The second method, called "acid process," is based on the catalytic action of hydroxonium ions, which even at low concentration produce solutions of low viscosities from native starch suspensions heated at 85°C for ½ hr. Both processes permit the use of reasonably high starch concentrations; hence, they lend themselves to large-scale industrial application. The mechanisms of both reactions are readily interpreted in the light of the unitary theory.

The Alkali Process of Starch Fractionation

In studying the properties of certain starch dispersions which will be discussed in Part VII of this series, we have found that no fractionation can be accomplished at room temperature by using an alkaline dispersion as such or after it has been neutralized with acid. However, on heating the neutralized solutions for a short time at a temperature above 60°C, a marked change in their viscosities takes place and, on subsequent cooling of the solutions in the presence of a complexing agent, excellent fractionation can be attained. In contrast to this behavior, which is characteristic of native starches, an artificial mixture of amylose and amylopectin can readily be separated by using either the unheated alkaline or the unheated neutralized solutions.

On the basis of these observations, an improved method of starch fractionation has been developed which utilizes starch dispersions prepared with dilute alkali. *A*- and *B*-fractions obtained by this technique are generally of a higher purity than those obtained by other commonly used fractionation methods. Amyloses resulting from autoclaving or from refluxing starch-water slurries will produce *A*-fractions which, before recrystallization, possess iodine absorption values less than 16%. These amylose complexes must, furthermore, be isolated by centrifugation at about 50,000 r.p.m. or greater. *A*-fractions from the refluxing process are often slimy and gelatinous [1].

On the other hand, fractionation by the new process, which shall be referred to as the "alkali process," always produced cornstarch *A*-fractions that readily formed dense, close-packed precipitates after centrifugation at only 2,000 r.p.m. These *A*-fractions exhibited iodine absorption values of about 16.5%, even before recrystallization. Preliminary experiments have revealed that successful alkali-process fractionation is achieved by dispersing 2% to 3% starch in 1*N* alkali, neutralizing the solution, and then heating it to about 90°C. Variable factors affecting the fractionation are: (*1*) concentration of the alkali in the dispersing medium, (*2*) pH of the solution that is to be heated, (*3*) concentration of starch in solution, and (*4*) heating time and temperature. Variable (*4*) will be discussed in Part VII of this series, so that attention is here focused on (*1*), (*2*), and (*3*), the other parameters of the alkali process.

The Effect of Alkali Concentration upon Dispersing Efficiency

Although 1*N* alkali solution will disperse starch sufficiently to permit efficient fractionation eventually, the solubility of starch in alkaline solutions

of lower concentrations was tested in order to determine whether dispersions capable of being fractionated could be prepared.

Because poor fractionation resulted from starch dispersions in 0.01*N* alkali, the fractionation process was repeated using 0.1*N* potassium hydroxide solution.

Experiment I.—At room temperature, 10 g. of dry, defatted cornstarch was mixed into 500 ml. of 0.1*N* potassium hydroxide solution. Because gelatinization did not take place at room temperature, the slurry was heated at 92°C for 1 hr. with 35 ml. of Pentasol to produce a clear dispersion. In order to establish that the dispersion was stable on standing, the liquid was refrigerated for 22 hrs. at 5°C. No change was evident after refrigeration. The solution was then neutralized and divided into two approximately equal volumes.

The first volume (*I*) was refrigerated overnight at 5°C and then passed through the Sharples Supercentrifuge at 12,000 r.p.m. No precipitate was deposited in the centrifuge rotor.

The second volume (*II*) was heated at 90°C for 1 hr. with constant stirring. It was then refrigerated at 5°C for 24 hrs., and finally was centrifuged at 2,000 r.p.m. to remove the *A*-fraction (*II–A*), which was washed twice with Pentasol-saturated water, the washings being added to the *B*-fraction solution. Two volumes of methanol precipitated the *B*-fraction (*II–B*) from solution. Yields and iodine absorption values are shown below.

Sample	Yield (% of total)	Yield (% of *II*)	Iodine absorption (%)
I	56	—	7.7
II-A	3	7	16.8
II-B	41	93	3.9

It is seen from these results that a 0.1*N* potassium hydroxide solution, unlike a 0.01*N* solution, disperses cornstarch with heating, so that no centrifugable material could be found in the neutralized dispersion. Nevertheless, heating the neutralized mixture for 1 hr. at 90°C failed to produce an efficient fractionation. Although an *A*-fraction of good purity was precipitated from the mixture, the *B*-fraction still contained large quantities of unliberated amylose.

Further increase of alkali concentration brought about an increase in fractionation efficiency, but, because the yields and the purities of the fractions were not as high as those resulting from fractionation with 1*N* alkali, the concentration of alkali was increased to 0.5*N*, as in the following experiment.

Experiment II.—A sample of 24.5 g. of dry, defatted cornstarch was rapidly stirred into 1,250 ml. of 0.5*N* postassium hydroxide solution at room temperature. After about 20–30 sec., a clear dispersion was obtained. To insure that dispersion was complete, the mixture was allowed to stand for 4 days and was then passed through the Sharples Supercentrifuge at 12,000 r.p.m. No precipitate was obtained. The clear solution was then used for fractionation as described in the following experiment.

Variation of Fractionation Efficiency with Varying pH

Experiment III.—The alkali dispersion in experiment *II* was divided into five aliquots of 250 ml. each, and these five volumes were titrated with 28% phosphoric acid to pH 4, 6, 8, 10, and 12, respectively. Each portion was saturated with Pentasol (18 ml.) and heated at 92°C under a nitrogen atmosphere for 1 hr. with constant stirring. When the mixtures had cooled, the pH of each was checked, and all samples were then refrigerated at 5°C. *A*-fractions were removed by centrifugation at 12,000 r.p.m. in the Sharples Supercentrifuge. Precipitates from pH 4, 6, 8, and 10 were firm and close-packed; the pH 12 *A*-fraction, however, was slimy and gelatinous. The changes in pH with heating, the yields of the fractions, and the iodine absorptions of the fractions are recorded in the table below.

pH		Yield (%)		Iodine absorption (%)	
Before heating	After heating	*A*-fraction	*B*-fraction	*A*-fraction	*B*-fraction
4.00	3.98	25.4	74.6	16.6	1.8
6.00	6.03	23.6	76.4	16.8	1.2
8.00	8.21	23.5	76.5	16.9	1.9
10.00	9.82	21.5	78.5	16.4	0.9
12.00	11.83	14.1	85.9	12.1	3.4

From these data, three conclusions may be drawn: (*1*) cornstarch may be fractionated efficiently starting from cold dispersions of starch in 0.5*N* alkali, (*2*) good separation of the fractions is obtained by heating the dispersions adjusted to from pH 4 to pH 10, and (*3*) the fractionation efficiency begins to decrease appreciably as the pH of the dispersion increases from pH 10 to pH 12. In another experi-

ment it was established that no fractionation occurs at pH 14.

The Effect of the Concentration of Starch on the Dispersion

All of the preceding examples of fractionation by the alkali process employed 2% aqueous starch dispersions. Indeed, no efficient fractionation of a starch dispersion which exceeds about 3% in starch concentration has been achieved by any known technique. It was anticipated that the excellent fractionation of 2% starch slurries that had been provided by the alkali process might be indicative of good separation at concentrations in excess of 2% starch. A step toward this goal, therefore, was the following alkali-process fractionation of a 5% starch slurry.

Experiment IV.—At room temperature, 25.1 g. of dry, defatted cornstarch was dispersed in 500 ml. of 1*N* sodium hydroxide solution. The mixture was acidified to pH 4 with 43% phosphoric acid, and was then heated at 92°C with 30 ml. of butanol for 5 hrs. After the mixture had been refrigerated overnight at 5°C, it was centrifuged at 12,000 r.p.m. in the Sharples Supercentrifuge to remove the *A*-fraction. The *B*-fraction was precipitated with two volumes of methanol. An analysis of the fractionation products is reported below.

Fraction	Yield (%)	Iodine absorption (%)
A	25	16.2
B	75	0.9

Both the purities and the yields of the *A*- and *B*-fractions were almost identical to those obtained from 2% starch dispersions.

Summary of the Alkali Process

Starch may be fractionated by the alkali process to yield about 24% *A*-fraction (iodine absorption of about 16%) and 76% *B*-fraction (iodine absorption of about 1% to 2%). The following is a general description of the alkali process of starch fractionation. Starch is dispersed in alkali solution at room temperature. The dispersion is neutralized and then heated at 92°C with an amylose-complexing agent. *A*-fraction is removed from the cooled solution by centrifugation at about 2,000 r.p.m. The basic parameters for efficient alkali-process fractionation are as follows:

Parameter	Limits
Alkali concentration in the starch dispersion	0.5*N* to 1.0*N* alkali, and probably higher concentrations
pH of the heated dispersion	pH 10 to pH 4, and perhaps lower pH's
Concentration of starch	about 5%
Heating time and temperature	disaggregation is complete within 3 min. at 60°C or higher (*cf.* Part VII)

The Acid Process of Starch Fractionation

The alkali process has made possible the fractionation of starch by using alkaline dispersions subsequently adjusted to between pH 4 and pH 10 and heated below 100°C. At concentrations of about 10%, however, the solutions were too viscous to permit good fractionation. Because one of the primary steps in fractionation seems to be the cleavage of highly acid-sensitive chemical bonds, increasing the hydroxonium-ion concentration below pH 4 might facilitate fractionation at higher starch concentrations. Pacsu and Hiller [3] noted that the yield of amylose from starch "appears to be a function of the concentration of H_3O^+ ions." They suggested that 0.1*N* sulfuric acid and organic acids, such as formic, citric, and acetic, will almost completely hydrolyze the hemiacetal (and possibly also acetal) starch bonds at 86°C. Nazarov [2] observed that the gelatinization temperature of potato starch was higher in hydrochloric acid solution than in distilled water. He attributed this behavior to a "weakening of the micelles" by the acid so that the fragments of the destroyed micelles are adsorbed on the "more highly polymerized components," thus forming larger aggregates. He did not, however, attempt to explain the nature of or differences between the micelles and the larger and "more highly polymerized components."

Pacsu [3] observed that if a slurry of 5% to 10% of starch in 0.1*N* acid is made, and the mixture is heated on a boiling water bath with constant stirring, it will set to a thick paste when the gelatinization temperature is reached. As the stirring is continued, the viscosity of the paste rapidly decreases until, in less than 1 hr., it reaches that of the original slurry.

The Effect of Starch Concentration

The first step in establishing optimum conditions for fractionation with the acid process consisted of

conducting a series of fractionations of different concentrations of starch, the concentration of acid and heating time being kept constant. In each case, butanol was added before heating to prevent retrogradation of the amylose.

Experiment V.—Samples of cornstarch were placed in 100 ml. of 0.1*N* hydrochloric acid with 20 ml. of butanol and heated in a boiling water bath. After 12 to 14 min., the temperature reached 85°C, where it was held constant. All samples were heated a total of 25 min. and then refrigerated overnight. The *A*-fractions were removed by centrifugation at 2,000 r.p.m. Yields and iodine absorption values are listed in the following table.

Conc. of starch in 100 ml. of acid (%)	Fraction	Yield (%)	Iodine absorption (%)
20.1	*A*	32.9	10.4
	B	67.1	0.3
17.1	*A*	32.4	10.0
	B	67.6	0.3
14.1	*A*	28.6	12.8
	B	71.4	0.2
12.1	*A*	26.7	14.2
	B	73.3	0.2

Because the iodine absorptions of the *A*-fractions were rather low, it was apparent that concentrations of starch above 12% were too high to permit a satisfactory separation of the components. Low iodine absorption values of the *B*-fractions seemed to indicate than an excessively long heating period or excessively high concentration of acid had been employed, resulting in degradation of the polysaccharide. On the other hand, the low iodine absorption values might indicate that extremely pure amylopectins had been obtained. Because the iodine absorption of the *A*-fractions increased rapidly as the starch concentration decreased from 14% to 12%, starch concentrations of 11% were used in further experiments.

The Effect of Heating Time

The next variable of the acid process to be studied was heating time.

Experiment VI.—Samples of 11 g. of starch in 100 ml. of 0.1*N* hydrochloric acid were each heated in a boiling water bath. In each case, gelatinization occurred after 2 min. of heating, and the temperature reached 85°C after an additional 7 min. Except in the case of the first sample, which reached only 82°C, each was held constant at 85°C after it had reached that temperature. Data are listed in the following table.

Total heating time (min.)	Fraction	Yield (%)	Iodine absorption (%)
8	—	no separation	—
12	*A*	33.0	11.1
	B	67.0	0.5
20	*A*	38.2	11.8
	B	71.8	0.2
35	*A*	26.4	13.4
	B	73.6	0.3
50	*A*	17.7	11.1
	B	82.3	0.7
60	*A*	19.8	9.9
	B	80.2	0.5

Because the sample heated 35 min. gave almost ideal yields (26.4% *A*-fraction and 73.6% *B*-fraction) and the resulting *A*-fraction was of higher purity than that of the other samples, 35 min. was chosen as the approximate optimum heating time for good fractionation under these conditions.

The Effect of Acid Concentration

The last important variable of the acid process to be investigated was acid concentration.

Experiment VII.—Using the values of starch concentration and heating time already selected by previous experimentation, the concentration of acid was varied in a series of fractionations. Each of the following samples consisted of 11 g. of defatted starch and 15 ml. of butanol in 100 ml. of acid solution. Gelatinization occurred after the mixtures had been heated 1.5 min. in the boiling water bath. After being heated 4.5 min., the samples reached 85°C, where the temperature was held constant for an additional 34 min. The containers were then removed from the bath and allowed to stand at room temperature for 1 day. *A*-fractions were centrifuged off at 2,000 r.p.m. The *B*-fractions were precipitated with two volumes of methanol; however, it was apparent that additional material remained in the supernatant solution. Neutralizing

and then concentrating the liquid by evaporation at 100°C permitted precipitation of the remainder of the *B*-fraction with methanol. This material was labeled B_2, whereas the initial *B*-fraction was labeled B_1. Data are recorded in the table below.

Acid conc.	Fraction	Yield (%)	Iodine absorption (%)
0.01*N*	—	no separation	—
0.03*N*	*A*	39.1	13.8
	B_1	60.2	0.9
	B_2	0.7	0.0
0.05*N*	*A*	29.4	15.5
	B_1	68.1	0.3
	B_2	2.5	0.0
0.07*N*	*A*	25.4	16.6
	B_1	71.4	0.0
	B_2	3.0	0.0

Fractions obtained from 0.07*N* hydrochloric acid were superior to any others obtained using acid concentrations of 0.01*N* to 0.1*N*. Therefore, this concentration was selected for optimum fractionation efficiency.

Summary of the Acid Process

Starch may be fractionated by means of heating with an amylose-complexing agent in a dilute solution of a strong acid. Investigation of the variables of this process has indicated that the following are optimum conditions for the hydrochloric acid-process fractionation:

Parameter	Limits
Starch concentration	11% or less
Heating time	35 min.
Acid concentration	0.07*N*

Characterization of the representative *A*- and *B*-fractions obtained from the alkali and acid processes is discussed in Part VI of this series.

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Manuscript received August 11, 1953.)

Starch Studies

Part VI. Characterization of Fractionation Products

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Introduction

Both the alkali process and the acid process of starch fractionation as described in Part V yield products which are readily identified, by iodine analysis, as *A*- and *B*-fractions. Although all *A*-fractions consist largely of amylose and the *B*-fractions of amylopectin, products resulting from one process may not necessarily be identical to those resulting from the other process. Whereas the alkali process might result in a mild attack on the starch granule without rupture of glucosidic bonds, the acid process could cause considerable hydrolysis of the glucosidic links. Thus, the polymers obtained from acid fractionation should be of lower molecular weight than those resulting from alkali fractionation. Nevertheless, if the disaggregation of the starch granules involves chiefly the rupturing of weak bonds, then products obtained from either process should possess the properties of *A*- and *B*-fractions obtained from autoclaved or boiled starch, and not those of so-called "dextrins," a term commonly employed to describe short-chain acid-degradation products of starch.

Molecular Weight Determinations

A number of experiments were undertaken in order to compare the molecular weights of fractions obtained from the acid process with corresponding ones obtained from the alkali process. Initial investigations proved that, unlike dextrins, *A*-frac-

tions from both processes were stained with iodine to a pure blue color and *B*-fractions from both processes were stained purple. These reactions are typical of amylose and amylopectin.

For a comparison of the molecular weights of materials resulting from the two methods of fractionation, three methods of estimation were employed: viscometry, end-group determination, and light scattering. Two large batches of starch were fractionated by the alkali process and by the acid process. The *A*-fraction obtained from the alkali process was recrystallized three times. All of the mother liquors from the recrystallizations were combined and added to the solution containing the *B*-fraction. Thus, no material was lost during fractionation. The *A*-fraction obtained from the acid process was recrystallized twice; the resulting mother liquors were also combined and added to the *B*-fraction to produce 100% recovery of starch. Iodine titrations of the four fractions gave the following results:

Fractionation method	Yield (%)		Iodine absorption (%)	
	A-fraction	*B*-fraction	*A*-fraction	*B*-fraction
Alkali	19	81	18.9	1.1
Acid	19	81	17.8	0.3

Viscometric Studies

Although viscometry has found widespread application in the starch industry, it has served mostly in the establishment of viscosity values for use as industrial standards. Reliable equations for the conversion of intrinsic viscosity values into molecular weights are unavailable. The Staudinger equation, M.W. $= K_m[\eta]^\alpha$, has received considerable popular support. The value of the exponent α is generally found to be 0.9 to 1.1 for solutions of cellulose in cuprammonium or cupriethylenediamine or of amylose in water. Accepting these values of α but not attempting to evaluate the constant K_m, it should be possible to compare the average molecular weight of one amylose with that of another. Because it is highly branched and not linear like amylose, amylopectin introduces further uncertainty into the applicability of the Staudinger equation.

We have determined the intrinsic viscosities of our starch fractions in 1*N* potassium hydroxide solutions in an effort to obtain a comparison between like fractions resulting from the two different methods of fractionation. It must be stressed, however, that no attempt was made to calculate molecular weights of any materials from the intrinsic viscosity values.

Experiment 1.—Approximately 0.2 to 0.6 g. of powdered starch-fraction sample was weighed and placed in a 25-ml. volumetric flask. To the powder approximately 15 ml. of distilled water was added, with shaking, to avoid the formation of lumps. This mixture was heated in a boiling water bath for 30 min., thus dissolving most of the starch. The mixture was cooled, and 5 ml. of 5*N* potassium hydroxide solution was added. After a lapse of 15 min., during which time all of the remaining solids had dissolved, the solution was diluted to 25 ml. to produce a dispersion of starch in 1*N* potassium hydroxide, and was then filtered through a plug of glass wool to remove any dust particles that might have been present. Dilutions were made with 1*N* potassium hydroxide.

Flow times were measured with a Cannon-Fenske type viscometer pipet of the No. 100 or No. 50 size. The flow times of each original sample and of two dilutions were determined at 25°C. Intrinsic viscosity, $[\eta]$, was obtained by plotting η_{sp}/c *vs.* concentration (c = g./100 ml.) on semi-logarithmic paper for the three concentrations of the sample, and by graphic extrapolation to zero concentration.

Fractionation	Fraction	Intrinsic viscosity
Alkali process	*A*	1.0
	B	1.0
Acid process	*A*	0.2
	B	0.1

The preceding data seem to indicate that the molecular weight of the *A*-fraction obtained by the acid process was only one-fifth that of the *A*-fraction obtained from the alkali process. If the Staudinger relationship is valid for amylopectin, then the molecular weight of the *B*-fraction from the acid process is only one-tenth that from the alkali process.

End-group Titrations

The determination by viscometric techniques of the relative molecular weights of the fractions was followed by secondary investigations for evaluation of the actual number-average molecular weights of

each of the four samples. Attention was directed toward the numerous techniques for the stoichiometric oxidation of the postulated reducing (aldehyde) end-groups of the polysaccharide chains, the reaction being represented by the following chemical equation:

$$R\text{—}CHO + 3OH^- + I_2 \rightarrow R\text{—}COO^- + 2I^- + 2H_2O.$$

Although several modifications of this titration technique were attempted, none yielded either consistent or reliable molecular weight values.

Experiment II.—The first technique to be applied was that of Gibbons [2], who oxidized samples of cellulose with a solution of iodine in a sodium carbonate-bicarbonate buffer solution at pH 10.6. The two *B*-fractions were titrated by this method. Approximately 350 mg. of *B*-fraction was weighed, placed in a 250-ml. titration flask with 40 ml. of water, and dissolved by heating. The solution was cooled, and 40 ml. of pH 10.6 buffer was added with 10 ml. of standard iodine solution (0.01*N*). The samples were refrigerated for 32 hrs. at 5°–8°C. They were then acidified with 6*N* hydrochloric acid and back-titrated with standard sodium thiosulfate (0.00536*N*). The results are as follows:

B-fraction from Acid Process

Sample (g.)	I_2 consumed (me.)	Molecular weight
0.3998	0.0861	92.9×10^2
0.3742	0.0838	89.3×10^2
0.3825	0.0823	94.0×10^2

The precision of the determinations was approximately 2%; however, the resulting number-average molecular weight value was only about 9,200. Corresponding to a degree of polymerization of only 57, this molecular weight seems too low in view of the physical properties of the material.

Subsequently, *B*-fraction from alkali fractionation was titrated by the Gibbons method, with some slight variations. Instead of being refrigerated for 32 hrs. immediately after the addition of iodine and buffer, the solutions were allowed to stand at room temperature for 30 min. and then were refrigerated for varying lengths of time in order to determine if a constant molecular weight value—indicating stoichiometric oxidation—could be obtained. Quantities of iodine, buffer, and hydrogen chloride solutions used were the same as those in the preceding titrations. The following results were obtained:

B-fraction from Alkali Process

Sample (g.)	Refrig. time (hrs.)	I_2 consumed (me.)	Molecular weight
0.3040	17	0.0755	176×10^2
0.3047	21	0.0782	278×10^2
0.3094	24	0.0717	219×10^2
0.3177	29	0.0724	244×10^2
0.3162	42	0.0748	250×10^2

The oxidation reaction is obviously unreliable, for the iodine consumption of the sample generally increases with increased reaction time. In addition, the sample which was refrigerated for 29 hrs. yielded an average molecular weight value of 24,400. This value is approximately 2.7 times that determined for the acid-process *B*-fraction (9,200) after 32 hrs. refrigeration. Viscosity determinations seemed to indicate that the alkali-process *B*-fraction should have an average molecular weight that is ten times the average molecular weight of the acid-process *B*-fraction.

In an endeavor to obtain more satisfactory end-group determinations, the method of Gibbons [2] was abandoned and that of Ingles and Israel [4] was employed. The essential difference between the two techniques lies in the selection of buffers and in the fact that the latter authors acidified the samples shortly after the addition of iodine instead of allowing the reaction to proceed over a period of hours. Whereas Gibbons oxidized his samples at pH 10.6, Ingles and Israel used a pH 11.4 buffer (25 ml. of 0.1*N* Na_2HPO_4 and 8.67 ml. of 0.1*N* NaOH, diluted to 50.0 ml.). More stable end-points were also obtainable by the bubbling of carbon dioxide through the solution toward the end of the titration with thiosulfate.

Experiment III.—Samples of *A*- and *B*-fractions were dissolved in 1*N* sodium hydroxide solution, allowed to stand at room temperature for some time to insure complete dispersion, and then neutralized with sulfuric acid. To each dispersion was added 5 ml. of standard (0.0211*N*) iodine solution and 25 ml. of pH 11.4 buffer solution. The mixture was allowed to stand at room temperature for 30 min. The samples were then acidified with 50 ml. of 3% sulfuric acid, and excess iodine was titrated with thiosulfate (0.01071*N*). The following results were obtained:

Acid Process

Sample (g.)	I_2 consumed (me.)	Molecular weight
A-fraction		
0.2761	0.0540	102×10^2
0.2679	0.0150	357×10^2
0.2627	0.0166	317×10^2
B-fraction		
0.2580	0.0572	90.2×10^2
0.2698	0.0589	91.6×10^2
0.3047	0.0612	99.6×10^2

Alkali Process

Sample (g.)	I_2 consumed (me.)	Molecular weight
A-fraction		
0.3053	0.0100	610×10^2
0.3070	0.0102	602×10^2
0.3035	0.0109	557×10^2
0.3042	0.0092	661×10^2
B-fraction		
0.3160	0.0460	137×10^2
0.3004	0.0416	144×10^2
0.3028	0.0339	179×10^2
0.3189	0.0402	159×10^2
0.3078	0.0166	371×10^2

The poor precision of the hypoiodite titrations has cast doubt upon the validity of the theoretical basis of this method of molecular weight determination—stoichiometric oxidation of reducing end-groups of polymer chains.

Light-Scattering Measurements

Comparison of the hypoiodite molecular weights of fractions from the two processes indicates that the *A*- and *B*-fractions from the alkali process had molecular weights about twice those of the corresponding fractions from the acid process. Viscometric data, however, seemed to contradict these relationships. The ratio of the intrinsic viscosity of the alkali-process *A*-fraction to that of the acid-process *A*-fraction was 5:1. The corresponding ratio of the intrinsic viscosities of the *B*-fractions from the two processes was 10:1. If the molecular weight of the polymer is directly proportional to its intrinsic viscosity, then the hypoiodite data were not in agreement with the viscometric data. For this reason, samples of the starch fractions were submitted for molecular weight determinations by light-scattering measurements.

Molecular weight values of three *B*-fractions, determined by light-scattering, were generously supplied to us by Dr. Lee P. Witnauer, of the Eastern Regional Research Laboratory, U. S. Department of Agriculture. Because dispersions of amylose in alkali seemed to exhibit abnormal scattering behavior, no *A*-fractions were analyzed.

In addition to the alkali-process and acid-process *B*-fractions which had undergone viscometric and hypoiodometric analyses, a third *B*-fraction was examined. This material, a product of the acid process, was selected because it possessed an iodine absorption of 0.0%.

The powdered, alkali-process *B*-fraction sample was dispersed in distilled water at 90°C for 15 min. to make an approximately 1.5% solution. Centrifugation of the sample at 17,000 r.p.m. produced little sedimentation. The treated solution was finally diluted with distilled water to the desired concentration and filtered through an ultrafine sintered-glass filter. Light-scattering measurements were made in the concentration range of 0.007% to 0.03%. After similar treatment of dispersion and clarification, both acid-process *B*-fractions were not visibly turbid at 1.5% concentration. Light-scattering measurements, therefore, were made in the concentration range of 1.5% to 0.4%, rather than 0.007% to 0.03%. Results are shown below.

B-fraction	Iodine absorption (%)	Average molecular weight
Alkali process	1.1	$67(\pm 20) \times 10^6$
Acid process	0.3	43×10^3
Acid process	0.0	120×10^3

Summary of Molecular Weight Determinations

Representative *A*- and *B*-fractions from both the alkali and the acid processes of starch fractionation were prepared and characterized by iodine absorption titrations, viscometric analysis, end-group analysis, and light-scattering measurements. Average values are shown in the following table.

Fraction	Iodine absorption (%)	Intrinsic viscosity [η]	End-group analysis (M.W.)	Light scattering (M.W.)
Alkali process				
A-fraction	18.9	1.0	61×10^3	—
B-fraction	1.1	1.0	22×10^3	$67(\pm 20) \times 10^6$
Acid process				
A-fraction	17.8	0.2	26×10^3	—
B-fraction	0.3	0.1	9.3×10^3	43×10^3

Experimental Procedures

Selection of Materials

Numerous varieties of starches are available in quantity, each differing slightly in size and shape but possessing similar properties. Applying all the experimental procedures to each species of starch would be an involved and seemingly endless task; consequently, one variety was selected for use in this investigation. Since this research program was carried out in an effort to elucidate the structure of starches in general, it was necessary to choose a representative sample, with the following general properties: granules of uniform size, to impart a sharp gelatinization temperature to the native material; low content of inorganic materials; and a composition of about 25% amylose and 75% amylopectin.

Cornstarch seemed to be the best choice; not only is it the most abundant starch in the United States, but also its other properties generally meet the above qualifications. The granules are uniform spheres of approximately 15μ diameter. Based on P_2O_5, the major inorganic constituent of nearly all starches, the phosphorus content is about 0.05%, in comparison to 0.2% for wheat and potato starches. Amylose and amylopectin exist in a ratio of 1:3, a distribution typical of most starch varieties.

With but a few exceptions, native cornstarch was used in all of the experiments.

Purification of Native Starch

Commercial cornstarch was defatted by refluxing in 85% methanol. One-hundred grams of starch was refluxed for 30 min. in 1 liter of 85% methanol, and the solid was removed by filtration. This process was repeated four additional times, producing clear washings. A sixth, and final, wash consisted of anhydrous methanol. The starch was filtered off, and then dried at 90°C and at about 10 mm. mercury pressure for 3 hrs.

Preparation of Fractionation Samples

A-fractions.—Each sample of wet amylose-complex was washed free of butanol (or Pentasol) and salts with 2:1 methanol-water solvent. This treatment was followed first by three soakings in absolute methanol to remove water, and then by three soakings in absolute diethyl ether to remove methanol. The samples were then dried at 90°C and at about 10 mm. mercury pressure for 3 hrs.

B-fractions.—In general, *B*-fractions were removed from *A*-fraction decantates by precipitation with two volumes of absolute methanol. If precipitation was incomplete, additional methanol or ether was added. Solids were centrifuged from the mixture, and washed and dried in a manner similar to that employed in the drying of *A*-fractions. *B*-fractions which formed hard lumps when washed with methanol were ground with a mortar and pestle before methanol-washing was continued.

Iodine Titration of Samples

The iodine absorptions of all samples were determined by potentiometric iodine titration using the apparatus devised by Higginbotham and Morrison [3], with a few modifications. Filter-paper plugs served satisfactorily in the salt bridge instead of sintered-glass plugs, and four-neck 250-ml. flasks were used instead of four-neck bottles.

The following stock solutions were necessary: (*a*) iodine solution consisting of 2 g. iodine, 37 g. potassium chloride (0.5*N*), 166 g. potassium iodide (1*N*), and distilled water to make 1 liter (the stock iodine solution was diluted to 10% strength for use); (*b*) 1*N* potassium iodide solution; (*c*) 1*N* potassium hydroxide solution; (*d*) 0.5*N* hydrochloric acid.

When the following procedure was adhered to, excellent precision ($\pm$ 0.1% iodine absorption) was readily achieved. Approximately 100 mg. of whole starch was weighed out for each analysis. If amylose was to be titrated, only about 50 mg. was used; and if amylopectin was to be analyzed, about 250 mg. was used. The weighed sample was placed in a small beaker and dissolved in 5 ml. of 1*N* potassium hydroxide. This starch solution was acidified to pH 4 (bromcresol-green end-point) with 0.5*N* hydrochloric acid, and 10 ml. of 1*N* potassium iodide was added. The mixture was washed into one of the titration vessels with 75 ml. of distilled water. A blank solution was prepared by the identical procedure, omitting the starch sample; it was placed in the other titration vessel. The two vessels were clamped into position. A platinum wire electrode, a stirrer, one end of the salt bridge, and the end of a 50-ml. buret were fitted into the necks of the titration flask containing the starch sample. The other four similar fixtures were inserted into the flask containing the blank solution, except that the

50-ml. buret was replaced by a 10-ml. microburet. Lead wires from the galvanometer were connected to the titration electrodes, closing the electrical circuit. Because the concentrations of iodine in both solutions were the same, the galvanometer read zero.

Both stirrers were started, and approximately 0.5 ml. of 1 : 10 stock iodine solution was run from the microburet into the blank solution, causing a deflection of the galvanometer. Iodine solution was then added to the starch solution from the 50-ml. buret until the galvanometer again indicated zero deflection. At this point, the redox potentials of the cells were equal because the concentration of free iodine *in solution* in each vessel was the same. The buret readings were recorded; and, beginning with the addition of another 0.5 ml. of iodine solution from the microburet, the procedure was repeated four additional times. Each time the galvanometer indicated zero redox potential, the concentrations of dissolved iodine were the same in each vessel. Whereas all of the iodine in the vessel containing the blank was in solution, the iodine in the vessel containing the starch was partitioned between two phases—the iodine in solution, and the iodine absorbed by the starch. In order to determine the quantity of iodine bound by the starch, one subtracts from the total quantity of iodine added to the starch solution the quantity of iodine added to the blank solution (which is equal to the quantity of dissolved iodine in the starch solution). Concentration differences caused by the change in the volumes of the two solutions are neglected. Milligrams of free iodine were plotted linearly against milligrams of bound iodine to obtain an essentially straight line, which was extrapolated to zero concentration of free iodine to yield the quantity of iodine bound by the starch. Since the weight of the sample was known, the bound iodine was expressed as a percentage of the sample weight—the so-called "Iodine Number."

This method of analysis offered a number of advantages over the commonly used potentiometric method [1] and over the Higginbotham and Morrison method [3]. Although the aforementioned authors indicated that the absorption of iodine by a starch solution is proportional to the logarithm of the concentration of free iodine in the solution, straight-line plots may be obtained on linear coordinates because there is little change in the quantity of iodine bound by the starch as the quantity of iodine in solution increases from 0.1 to 0.5 mg. (0.5 to 2.5 ml. of iodine titrating solution). Tabulation was simplified by the standardization of the stock solutions to the exact concentrations specified. Thus, milliliters of iodine solutions were converted into milligrams of iodine by multiplying the former value by 0.2. A typical graph of an amylose and amylopectin titration is shown in Figure 1. Typical data are given below.

Iodine Absorption Titration of an A-Fraction

Sample = 0.0484 g.

Iodine added				Iodine absorbed (difference between sample and blank)
Sample		Blank		
(ml.)	(mg.)	(ml.)	(mg.)	(mg.)
41.94	8.388	0.70	0.140	8.248
43.02	8.604	1.12	0.224	8.380
44.20	8.840	1.70	0.340	8.500
45.08	9.016	2.00	0.400	8.616
46.20	9.240	2.50	0.500	8.740

% Absorption = 8.05/48.4 × 100 = 16.6%

Iodine Absorption Titration of a B-Fraction

Sample = 0.2573 g.

Iodine added				Iodine absorbed (difference between sample and blank)
Sample		Blank		
(ml.)	(mg.)	(ml.)	(mg.)	(mg.)
18.84	3.768	0.70	0.140	3.628
22.07	4.414	1.00	0.200	4.214
26.83	5.366	1.50	0.300	5.066
31.71	6.342	2.00	0.400	5.942
36.51	7.302	2.50	0.500	6.802

% Absorption = 2.40/257.3 × 100 = 0.93%

Conclusions

Application of standard methods of molecular weight estimations to representative *A*- and *B*-fractions from both the alkali and acid processes of

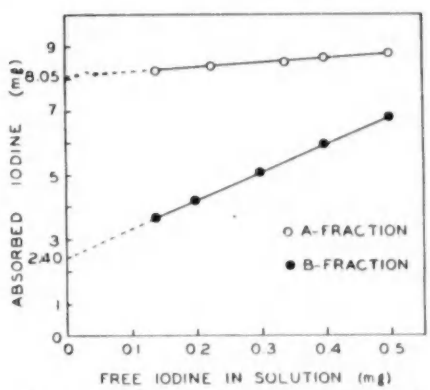

FIG. 1. *Absorption of iodine in A- and B-fractions of cornstarch.*

starch fractionation has failed to yield consistent results. Particularly striking is the high value, sixty-seven million, obtained by light-scattering measurement on the alkali-process *B*-fraction. In spite of the large deviations in molecular weights of the products, the alkali process, in general, gives rise to fractions with higher values than does the acid process. Both methods have produced fractions possessing properties sharply different from those of the so-called "dextrins" but similar to those of the conventional *A*- and *B*-fractions. Since the considerable decrease in viscosities experienced on heating the neutralized starch dispersions seemed to be the result of a disaggregation process which permitted fractionation, an investigation of this phenomenon has been undertaken, the results of which are presented in Part VII of this series.

Acknowledgment

The authors wish to express their appreciation to Dr. Lee P. Witnauer, Eastern Regional Research Laboratory, U. S. Department of Agriculture, for carrying out the molecular weight determinations by the light-scattering method.

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(Manuscript received August 11, 1953.)

Starch Studies

Part VII. Properties of Starch Solutions and the Kinetics of Starch Disaggregation

Albert W. Bauer and Eugene Pacsu

Introduction

From a theoretical view, starch solutions may originate in one of two possible ways. Those who have adopted the multiple concept believe that native starch may be dissolved in a solvent by simply dispersing the amylose and the amylopectin constituents in the solution medium. The resulting dispersion will, therefore, exhibit the properties unique to each polymer. Proponents of the unitary concept believe that starch molecules suffer hydrolysis during dissolution treatment, producing artifacts—amylose and amylopectin.

If the multiple concept of starch structure is valid, two arrangements of the components in the granules are possible: either amylose and amylopectin form a solid solution, or they exist in separate parts of the granule. Two cohesive forces—hydrogen-bonding and molecular entanglement—might play major roles in providing stability to this granule structure, but dissolution of the granules would involve merely rupturing of hydrogen bonds and perhaps disentangling of the molecules.

Proponents of the unitary theory believe that chemical bonds are ruptured during the disaggregation process. Indeed, a review of the methods of fractionation [11, 14] reveals that, without exception, every method of starch fractionation follows a pretreatment involving the heating of the starch in water to a temperature of 60°C or greater. In spite of the basic differences of opinion concerning the process which takes place during the heating stage, no one had attempted to prepare for fractionation a solution of starch which would eliminate this drastic treatment. If the unitary concept were correct, a molecular dispersion of native starch in any solvent would contain starch molecules, not amylose and amylopectin molecules, and the solution would possess the identical properties of neither of these two polymers. On the other hand, if the multiple concept were valid, amylose and amylopectin would exist freely in solution, each exhibiting its character-

istic properties, and a separation of the two components would be a simple process by any of the common methods of fractionation.

Investigation of Starch Solution Properties

Alkali has frequently been used in the preparation of starch dispersions for iodine titrations and similar manipulations. In sodium or potassium hydroxide solutions, native starch may be dispersed at room temperature, the resulting dispersion being optically clear when viewed through bright-field microscopes. The authors have observed that the addition of butanol, Pentasol, or any of the common amylose precipitants to such an alkaline starch solution will *not* produce precipitation.

Moreover, caustic starch solutions may be neutralized with acid to yield stable dispersions that also are optically clear, but cannot be fractionated by the addition of amylose precipitants. Neutral salts, such as sodium chloride or potassium phosphate, for example, are the only inorganic constituents of these neutral solutions, and should have no appreciable effect on the complexing properties of the starch constituents.

Attempts to explain the behavior of starch in alkaline solution have uncovered numerous independent phenomena. Although these investigations [9, 13, 21] have indicated that strong alkali may slightly modify starch, none of the observed behavior suggests an appreciable alteration of the structure of the starch. The material that results from the neutralization of a cold alkali starch dispersion is, then, nearly identical in chemical structure to the undissolved starch. Without heating the mixtures, we have produced clear, homogeneous starch solutions with alkali concentrations as low as 0.5*N*. The granules could readily be dispersed in 0.1*N* alkali when heated to the gelatinization temperature, but heating was insufficient to disperse completely the starch in 0.01*N* caustic. That a starch dispersion made by dissolving native starch in caustic cannot be fractionated without the neutralized solution first being heated is demonstrated in the following experiment.

Experiment 1

Samples of cornstarch were dissolved at room temperature in 1.0*N* alkali to make a 2% to 3% solution. The solution was neutralized to about pH 7 with concentrated hydrochloric acid, and butanol or Pentasol was added to saturation. No precipitates could be obtained, even when the mixtures were passed through the Sharples Supercentrifuge at 12,000 r.p.m. Similar starch dispersions, titrated with phosphoric acid to pH 4 and pH 10, also did not produce any precipitation. Furthermore, within the times of observation these dispersions remained stable, even at temperatures as low as 5°C and not higher than 30°C.

However, a marked change took place when such neutral dispersions were heated to 90°C with butanol or Pentasol. As the mixture was cooled, a precipitate began to settle to the bottom of the vessel. From pH 7 mixtures, precipitation was complete in about 5 hrs., and the solid material was removed from the supernatant solution by centrifugation at 2,000 r.p.m. After being dried and titrated with iodine, the product was found to be amylose, having an iodine absorption value of about 16%. The decantate contained amylopectin that was contaminated with a small quantity of amylose. (Subsequently, any butanol or Pentasol precipitate will be referred to as the "*A*-fraction" [14, 15] and the starch remaining in solution as the "*B*-fraction.")

As previously suggested, two forces might possibly inhibit the separation of the two starch components. The first, hydrogen-bonding, seems hardly likely to be an appreciable factor after an alkali treatment, but molecular entanglement could conceivably tie the chains to one another. If this were true, then the crucial heating step, which permits fractionation, would involve the addition of sufficient energy to disentangle the amylose and amylopectin chains. In other words, heating of a starch dispersion would, then, merely complete the disintegration of the starch granule structure and release amylose and amylopectin, as would be predicted by the multiple concept of starch structure. A simple test of this explanation, therefore, would be to heat an alkaline starch dispersion *before* neutralizing it. Any hydrogen-bonding which causes molecular association should be readily broken in the hot strong alkaline solution, and the molecules should become disentangled. If, after the alkaline starch solution has been heated and neutralized, saturation of the solution with butanol does not precipitate amylose, then the amylose and amylopectin are most likely united by some alkali-resistant, covalent chemical bonds. The following experiment was carried out in order to gain information regarding the validity of this conclusion.

Experiment II

Ten grams of cornstarch was dispersed in 500 ml. of 0.10*N* potassium hydroxide solution, and 35 ml. of Pentasol was added. The mixture was placed in a nitrogen atmosphere and heated to 92°C for a period of 4 hrs. with constant stirring. Stirring was continued for 15 hrs. while the mixture was allowed to cool. Hydrochloric acid was added to a phenolphthalein end-point, and the resulting solution was then refrigerated at 5°C for 48 hrs. No precipitate could be removed on the Sharples Supercentrifuge.

Since separation could be achieved neither from heated caustic dispersions even after neutralization nor from unheated neutralized dispersions, it is apparent that this behavior is due either to some anti-complexing agent present in the solution or to chemical bonding between the amylose and the amylopectin. These starch solutions differ in composition from those commonly employed in the butanol and Pentasol fractionation of starch only by the presence of simple inorganic salts. Although it seemed unlikely that the salts could have an appreciable effect upon the complexing properties of the starch in solution, this possibility was tested by conducting a separation in a slurry containing normal postassium chloride, according to the method of Lansky, Kooi, and Schoch [12]. The yields and iodine absorption values of the fractions obtained proved that the salt was ineffective in inhibiting the fractionation of starch.

For verification of our previous conclusion that the inseparability of the unheated neutral starch solutions is most likely caused by chemical bonding in the native material, an artificial mixture of amylose and amylopectin was treated according to the alkali dispersion procedure. If the behavior of the native starch in the caustic and the neutralized solutions was an effect of the composition of the solutions and not a characteristic of natural starch, then an artificial mixture of amylose and amylopectin would exhibit the same behavior as native starch under these conditions—it would not separate into the components. The experiment was carried out as follows.

Experiment III

A mixture consisting of 3.24 g. of amylose (iodine absorption 15.5%) and 7.00 g. of amylopectin (iodine absorption 1.03%) was dissolved in 500 ml. of 1*N* potassium hydroxide solution and allowed to stand for 3 days. The resulting solution was divided into two equal volumes of 250 ml. which were titrated with 12*N* phosphoric acid, one to pH 4 and the other to pH 10. Each solution was saturated with 30 ml. of butanol. After being stirred intermittently for 24 hrs., the two solutions were centrifuged at 2,000 r.p.m. *A*-fractions were removed from both of the solutions; however, precipitation from the solutions having pH 10 was complete only after the mixture had stood for 6 additional days. The first precipitate of *A*-fraction from the latter was labeled *A–1*, the balance of the *A*-fraction being *A–2*. The following table gives the results obtained:

Sample	Yield (%)	Iodine absorption (%)
A-fraction (pH 4)	26.9	14.1
B-fraction (pH 4)	73.1	1.8
A-1-fraction (pH 10)	11.2	15.9
A-2-fraction (pH 10)	13.6	17.6
B-fraction (pH 10)	75.2	1.8

There can be no doubt that the artificial mixture was fractionated in spite of the fact that the solution was never heated above room temperature. It was noted that *A*-fraction precipitations from solutions having pH 10 always required excessively long precipitation periods whether the samples were artificial mixtures of amylose and amylopectin or whether they were native starch dispersions that had been neutralized and heated. It is, however, unlikely that this behavior is of any significance other than to suggest that the rate of precipitation of the amylose complex decreases with increasing pH.

Kinetics of Disaggregation

The simplest explanation of the experimental results obtained in our investigation would be that amylose and amylopectin in native starch are joined to each other by chemical bonding to form starch molecules, which are soluble in caustic solution. These links would exist in the native starch, but would be at least partly eliminated when the starch is heated in water solution. One must, then, turn to the unitary concept for a satisfactory explanation of the nature of these chemical bonds. All of the prominent theories of the unitary concept describe types of linkages which are acid-labile. Although the presence of alkali-labile starch cross-links has not been given much serious consideration, the preceding experiments have provided strong additional

evidence that the disaggregation process is not a function of the rupturing of alkali-sensitive bonds. Starch which was heated at 92°C in alkali for several hours could not be fractionated upon neutralization. Certainly, under these conditions, ester or other alkali-labile bonds would be ruptured.

From the information which has been accumulated in the preceding experiments, only three important facts are known concerning the identity of the amylose-amylopectin bond: (*1*) the bond may be ruptured by hydrolysis, (*2*) the hydrolysis is catalyzed by protons, and (*3*) the hydrolysis occurs at a temperature well below 100°C. Of these facts, (*3*) had been investigated the least. The next logical step in the investigation, then, was to determine the temperature limits of the hydrolysis reaction—that is, the maximum temperature at which a neutralized alkali starch solution is stable, and the minimum temperature at which the hydrolysis would take place rapidly.

A neutral starch solution was prepared by the alkali-dispersion technique, and the temperature of the solution was raised to a given value and held constant. Because hydrolysis of the polymer involves a decrease in the molecular weight of the material, measurement of the viscosity of the solution was selected as a convenient criterion of change in molecular weight at constant temperature.

Experiment IV

The following solutions of dry, defatted cornstarch were prepared: (*a*) 0.512 g. of starch dissolved in 25 ml. of 1*N* potassium hydroxide solution at room temperature, neutralized with 0.5*N* hydrochloric acid, and diluted to 100 ml. (conc. 0.512 g./dl.); (*b*) 3.05 g. of starch dissolved in 62.5 ml. of 1*N* potassium hydroxide solution at room temperature, neutralized with 0.5*N* hydrochloric acid, and diluted to 250 ml. (conc. 1.22 g./dl.).

An aliquot of 5.00 ml. of the starch solution (*a*) was placed in a No. 100 Cannon-Fenske viscometer pipet, and the pipet was immersed in a 60° ± 0.05°C constant-temperature bath. Immediately the solution was drawn into the upper bulb of the pipet, and the flow time of the solution was measured. At frequent intervals the flow time was checked, and the total time from the immersion of the pipet was recorded with each flow time. Except for the small initial change in flow time (immersion for about 3 min. was necessary for the solution to come to thermal equilibrium with the bath), no change in the viscosity of the solution was apparent after the first measurements had been taken at 60°C.

This process was then repeated at 50°C and at 40°C, a fresh aliquot of solution being used on each run. At these temperatures, solution (*b*) was employed, since the higher starch concentration produced longer flow times and, therefore, greater precision of measurement. The solution flow time, specific viscosity, and reduced viscosity were recorded for each accumulative time at 40°C, 50°C, and 60°C (Tables I, II, and III).

From these data it is readily apparent that at 40°C a slow disaggregation of the starch was effected.

TABLE I. VISCOSITY CHANGE OF A STARCH SOLUTION AT 40°C
(FLOW TIME OF SOLVENT = 52.1 SEC.; CONC. = 1.22 G./100 ML.)

Accumulative time (min.)	Flow time (sec.)	Specific viscosity η_{sp}	Reduced viscosity $\eta_{sp}/conc.$	Rate of disaggregation $10^5 \cdot k = \frac{1}{t}(1/\eta'_2 - 1/\eta'_1)$
45	140.5	1.696	1.390	—
166	140.2	1.690	1.385	2.15
430	139.3	1.673	1.371	2.80
1170	136.9	1.627	1.334	2.73
1460	136.0	1.610	1.320	2.76
1980	134.7	1.584	1.298	2.46
2570	133.4	1.560	1.279	1.96
3300	131.8	1.529	1.253	2.20
4040	130.3	1.500	1.230	2.01
4400	129.5	1.485	1.217	2.41
5470	127.5	1.447	1.186	2.01
5830	126.9	1.435	1.176	1.97

Average $k = 2.33 \times 10^{-5}$ min.$^{-1}$ (3.89×10^{-7} sec.$^{-1}$)

It occurred at a more rapid rate at 50°C, and was complete after only 5 min. at 60°C. Thus, any method of starch fractionation which includes the heating of a starch dispersion in water involves a certain degree of degradation of the starch.

In order to gain some information as to the nature of the degradation reaction, we have investigated the kinetics of this process. Freudenberg, Kuhn, and coworkers [6, 7, 8] studied the homogeneous degradation of various polysaccharides under controlled conditions. Later, af Ekenstam [2, 3, 4] and Stamm and Cohen [17] investigated the degradation of cotton and wood pulps in phosphoric acid solution by determining the changes in viscosity.

In all these studies it was assumed that the degradation takes place as a first-order, unimolecular

TABLE II. VISCOSITY CHANGE OF A STARCH SOLUTION AT 50°C
(FLOW TIME OF SOLVENT = 44.8 SEC.; CONC. = 1.22 G./100 ML.)

Accumulative time (min.)	Flow time (sec.)	Specific viscosity η_{sp}	Reduced viscosity η_{sp}/conc.	Rate of disaggregation $10^2 \cdot k = \frac{1}{t}(1/\eta'_2 - 1/\eta'_1)$
1.00	116.6	1.603	1.314	—
3.58	109.9	1.453	1.191	3.046
8.33	106.6	1.379	1.130	0.955
10.5	104.0	1.321	1.083	1.770
12.4	102.0	1.277	1.047	1.668
14.8	100.4	1.241	1.017	1.175
17.1	98.7	1.203	0.986	1.343
19.1	97.5	1.176	0.964	1.155
21.2	96.7	1.158	0.949	0.800
23.2	95.0	1.120	0.918	1.775
26.2	93.8	1.094	0.897	0.856
27.5	92.7	1.069	0.876	2.061
29.5	91.6	1.045	0.857	1.260
31.5	90.7	1.024	0.839	1.250
33.6	89.9	1.007	0.825	0.952
35.6	88.8	0.982	0.805	1.510
37.6	88.0	0.964	0.790	1.165
39.7	87.1	0.944	0.774	1.262
41.6	86.5	0.931	0.763	0.978
43.6	85.7	0.913	0.748	1.320
45.6	85.1	0.899	0.737	1.000
47.1	84.5	0.886	0.726	1.360
49.3	84.0	0.875	0.717	0.786
51.4	83.3	0.859	0.704	1.230
53.3	82.8	0.848	0.695	0.973
55.1	81.8	0.815	0.668	3.220
59.0	80.8	0.803	0.658	0.584
60.8	80.3	0.792	0.649	1.180
62.6	80.1	0.788	0.646	0.400
64.6	79.5	0.774	0.634	1.515
78.1	76.5	0.707	0.580	3.930
104	72.1	0.609	0.499	1.081
146	67.7	0.511	0.419	—
183	65.1	0.453	0.371	—
354	60.2	0.344	0.282	—
412	59.6	0.330	0.271	—
450	59.3	0.324	0.266	—
570	58.5	0.306	0.251	—
1300	55.1	0.230	0.189	—
1440	54.3	0.212	0.174	—
1470	54.2	0.210	0.172	—
1650	53.7	0.199	0.163	—
2920	52.1	0.163	0.134	—
4500	51.1	0.141	0.116	—
6400	50.6	0.129	0.106	—
7020	50.2	0.120	0.098	—
				Average $k = 1.42 \times 10^{-2}$ min.$^{-1}$ (2.36×10^{-4} sec.$^{-1}$)

reaction, as expressed by the equation

$$\frac{dn}{dt} = -kn, \qquad (1)$$

where n is the mole of bonds in 1 liter capable of undergoing cleavage, t is the time of degradation, and k is the degradation constant.

By introducing the degree of polymerization (D.P.) in this equation, af Ekenstam [2, 3, 4] and, later, Schulz and Löhmann [16] arrived at the following expression for the degradation constant:

$$k = \frac{1}{t} \ln \frac{(1 - 1/\text{D.P.}_o)}{(1 - 1/\text{D.P.}_t)}. \qquad (2)$$

Af Ekenstam has shown that this equation is equivalent to that used by Freudenberg and Kuhn in their work.

In our investigation we have assumed that the decrease in viscosities of the starch dispersions on heating is caused by random rupture of some chemical bonds in starch, that it represents a direct measure of the progress of the degradation, and that equation (2) is applicable to the process. The rate constant is then calculated from the equation

$$k = \frac{1}{\Delta t} (1/\eta'_2 - 1/\eta'_1), \qquad (3)$$

where $1/\eta'_1$ and $1/\eta'_2$ are the "reduced fluidities" (reciprocal values of η_{sp}/c), determined at consecutive intervals of time, Δt, in the samples kept at constant temperature.

It is to be noted that equation (3) represents the leading term of the expansion of the logarithmic expression

$$k = \frac{1}{t} \ln \frac{(1 - 1/\eta'_1)}{(1 - 1/\eta'_2)}, \qquad (4)$$

which corresponds to equation (2), where the viscosity values are multiplied by some conversion factor to introduce molecular weights or D.P. values (D.P. $= \eta' K_m$). The expression containing the latter values,

$$k = \frac{1}{t} (1/\text{D.P.}_t - 1/\text{D.P.}_o), \qquad (5)$$

has been used in various forms by numerous investigators [1, 2, 3, 4, 10, 18] to calculate the rate constant for both the homogeneous and heterogeneous degradation of cellulose.

Use of equation (3) in the present investigation is assumed to be justified, since the progress of the reaction is followed only at the early stage, as evidenced by the relatively small extent of change between the initial and final values of η_{sp}/c.

The values for k calculated from equation (3) giving the rate of disaggregation between $\eta_{sp}/c =$ 1.387 and 1.176 at 40°C, and between 1.314 and 0.499 at 50°C, are shown in the last columns in Tables I and II. It is seen that the k values remain reasonably constant within the specified ranges, giving $k_{40} = 2.33 \times 10^{-5}$ min.$^{-1}$ and $k_{50} = 1.42 \times 10^{-2}$ min.$^{-1}$, or $k_{40} = 3.89 \times 10^{-7}$ sec.$^{-1}$ and $k_{50} = 2.36 \times 10^{-4}$ sec.$^{-1}$. The constancy of the k values has been confirmed by plotting the differences in the $1/\eta'$ values against time, and obtaining a straight line.

The most striking result of these measurements is the fact that the increase in rate of reaction when the temperature is raised 10°C is 600 instead of being 2 or 3, as is usually the case. This clearly puts the type of reaction in the category represented by the denaturation of proteins and the inactivation of enzymes or hormones [5].

From the integrated form of the Arrhenius equation,

$$E = R \frac{T_1 T_2}{\Delta T} \ln \frac{k_{50}}{k_{40}}, \qquad (6)$$

the energy of activation is calculated to be $E = 128.7$ kcal., or, since $\Delta H^{\ddagger} = E - RT$, the heat of activation, $\Delta H^{\ddagger} = 128$ kcal.

Substitution of this value in the Eyring equation [20],

$$k_{40} = \frac{K_a T}{h} e^{-\Delta H^{\ddagger}/RT} e^{\Delta S^{\ddagger}/R}, \qquad (7)$$

gives the entropy of activation, $\Delta S^{\ddagger} = 320$ e.u.; hence, the free energy of activation, $F^{\ddagger} = 27.8$ kcal.

In view of the enormously high heat of activation, it is not reasonable to conclude that starch disaggregation is caused by the cleavage of some extra-

TABLE III. VISCOSITY CHANGE OF A STARCH SOLUTION AT 60°C (FLOW TIME OF SOLVENT = 39.6 SEC.; CONC. = 0.512 G./100 ML.)

Accumulative time (min.)	Flow time (sec.)	Specific viscosity η_{sp}	Reduced viscosity η_{sp}/conc.
1.50	59.9	0.516	1.008
2.50	56.6	0.433	0.846
3.67	56.5	0.430	0.840
5.00	56.4	0.427	0.834
8.67	56.5	0.430	0.840
39.12	56.5	0.430	0.840
63.33	56.5	0.430	0.840

ordinarily strong covalent bond in a long-chain molecule. In other words, starch solutions, commonly used for so-called "molecular weight determination," do not consist of molecularly dispersed, single amylose and amylopectin chains. It is more reasonable to assume that starch in solution consists of giant aggregations of highly solvated, three-dimensional bundles or micelles of single-chain molecules held together by weak, acid-sensitive, hemiacetal (acetal) or phosphatide cross-links. By the simultaneous cleavage of a set of such relatively weak covalent bonds, a great number of the bound water molecules "melt away," and the originally rigid configuration of the aggregations opens up, with a resulting loss of structure or a large increase in randomness.

It is not proposed that such a process necessarily results in molecularly dispersed single-chain molecules; a good many of the assumed cross-links, however weak they may be, are probably situated in some critical, inaccessible regions, and their ultimate scission should occur only in the event of further hydrolytic degradation strongly catalyzed by hydroxonium ions.

Three types of acid-labile starch bonds have been postulated: glucosidic bonds, open-chain acetal bonds, and phosphatide cross-links. Reasons why it is extremely unlikely that the disaggregation process is a function of the hydrolysis of normal glucosidic bonds have been discussed in Part IV; supporting evidence for this conclusion is now seen in the abnormal thermodynamic data obtained. Attention is then focused on the open-chain acetal (hemiacetal) and phosphatide bonds. A final selection between these two types of chemical bonds has not been achieved. No method has been devised as yet for the direct analysis of acetal bonds. Furthermore, direct analysis of the phosphatide links by titrating the free acid groups liberated during hydrolysis is hampered by the fact that only a very small quantity of phosphate is present in the starch. It must be noted, however, that in view of the stability of starch in caustic, the original phosphate cross-link theory proposed by Sutra [19] must be revised. Sutra suggested that the phosphate ester groups bonded to the amylopectin, for example, are cross-linked to the reducing end-groups of the amylose chains, forming phosphatide bonds. However, solutions of starch in strong alkali are stable when heated, a treatment which would hydrolyze phosphate esters and, therefore, destroy the cross-link. Thus, if phosphate groups provide the cross-links between amylose and amylopectin, each amylose must be joined at the reducing end-group to a phosphate which is bonded to the reducing end-group of an amylopectin molecule, producing an alkali-resistant, but acid-sensitive, diphosphatide structure. After normal starch fractionation, however, all phosphate groups are found to be amylose or amylopectin phosphate esters. Therefore, if phosphatide cross-links unite the starch components, then all of the three valences of starch phosphates are employed—one as an ester, and the other two as phosphatides (Figure 1).

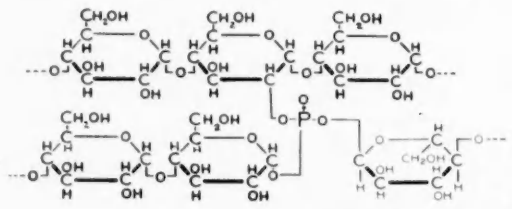

FIG. 1. *Modified phosphate cross-link, according to Sutra.*

The authors are aware of the speculative nature of this theory, and they propose it only as a rationalization of the thermodynamic data, which, assuming that the underlying equation (3) is valid and applicable to starch disaggregation, cannot be understood on the basis of the hitherto accepted theory of molecular chain structure in solution.

The disaggregation reaction appears to be dependent upon the pH of the environment, and this aspect of the problem needs further quantitative investigation.

Summary

Native cornstarch was dispersed in alkali to produce solutions that were stable and optically clear even after the mixture had been neutralized with acid. The addition of an amylose-complexing agent, such as butanol or Pentasol, did not precipitate amylose complex from the solution. A prepared mixture of amylose and amylopectin was dispersed in alkali and neutralized to produce a clear dispersion. The addition of a complexing agent to this dispersion caused the amylose to precipitate from solution as an amylose complex. When a neutralized native starch dispersion was heated to 60°C or higher, the addition of an amylose-complexing agent caused the precipitation of amylose complex—the identical re-

sult that was observed with the prepared mixture of amylose and amylopectin.

A similar dispersion of starch in alkaline solution was first heated and then neutralized, but the addition of an aymlose-complexing agent failed to induce precipitation.

These phenomena were not caused by the presence of salts (resulting from the neutralization of the dispersing alkali) in the solutions. Removal of salt by the use of an ion-exchange resin produced no change in the behavior of the solution. Furthermore, starch that had been refluxed in 1.0*N* salt solution was readily fractionated.

It was concluded that, in native starch, amylose and amylopectin are bound together to form starch molecules. When neutral starch dispersions were heated above 60°C, the amylose-amylopectin bonds were hydrolyzed, liberating the two starch components. Because heating alone of an alkaline starch dispersion did not make the starch capable of being fractionated, it appeared that the hydrolysis of the amylose-amylopectin bonds was catalyzed by the hydroxonium ion. Of the several amylose-amylopectin bond structures that have been postulated, two of these structures possess properties which correspond to the properties of the amylose-amylopectin bonds: phosphatide bonds and open-chain hemiacetal or acetal bonds. From the abnormally high thermodynamic data, it was concluded that the process of disaggregation is caused by the simultaneous rupture of a set of such weak bonds, resulting in an "opening up" of the originally rigid aggregations, and in the loss of the native structure.

Acknowledgment

This work was carried out as a part of the general research program of Textile Research Institute. One of us (A. W. B.) is grateful to Textile Research Institute for the fellowship grant which made this work possible.

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(Manuscript received August 11, 1953.)

"*S* Factor," A Microbial Enzyme which Increases the Swelling of Cotton in Alkali

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Abstract

Exposure of cotton fiber to cell-free filtrates obtained from certain culture media after the growth of microorganisms increases the degree of subsequent swelling of the fiber in NaOH solutions. The active agency in the filtrates is here termed "*S* factor." Its action is measured by a previously described alkali-centrifuge test [12].

With the fungus *Myrothecium verrucaria*, *S* factor was produced during growth in media which included any of several cellulose-containing materials but not in any of several media lacking in cellulose. This finding and related results suggest that *S* factor consists at least in part of an enzyme or enzymes of the cellulase complex. A simple and reliable method of preparing *Myrothecium* filtrates of uniform and high *S* activity is reported.

Several properties of *S* factor in *Myrothecium* filtrates have been observed. It is operative over a wide pH range. A very considerable uptake of the factor from solution by cotton fiber and a major increase in alkali-centrifuge value of the fiber occur in 10 min. Strength losses take place much more slowly. *S* factor is moderately stable in sterile filtrates at room temperature. Filtrates may be stored in frozen condition or may be dried at 40°C and stored dry with little loss in activity. The active factor is precipitated by acetone and is inactivated by crystalline pepsin.

Although partial inactivation of *S* factor by heat occurred in ½ hr. at temperatures of 60°C and higher, complete inactivation did not take place even at much higher temperatures, and easily measurable activity remained even after heating at 100°C for ½ hr. Autoclaving at 15 lbs. steam pressure for 15 min. caused complete inactivation. The same filtrates also exhibited resistance to complete cellulase inactivation by heat when tested by a carboxymethylcellulose-viscosity test for cellulase.

IT has been known for many years that the growth of microorganisms on cotton fiber commonly results in microscopically visible increases in the degree of swelling of the fiber in alkaline solutions [10, 19]. This effect was measured recently by a new centrifuge-weight increase method for determining the degree of alkali-swelling of cotton fiber [12]. By the same method not only microbial growth but also exposure to filtrates from microbial growth media was found to increase subsequent alkali-swelling [12]. The agency in the filtrates which causes this effect is here termed "*S* factor," and certain experiments relating to its production and properties are described.

Blum and Stahl [2] noted that filtrates from the growth medium of the fungus *Myrothecium verrucaria* bring about a microscopically visible increase in the subsequent swelling of cotton fiber in copper ethylenediamine. They considered this increased swelling to be a result of enzymatic degradation of the outer wall of the fiber, with a consequent decrease in the restrictive effect which this wall normally exerts on alkali-swelling. The degradation of the outer wall was also evidenced by increased absorption of Congo red and by the progressive disappearance of the "winding layer."

Methods

The general method for determining *S* activity was to measure the alkali-centrifuge value [12] of a test cotton fiber after exposure under certain standardized conditions to a growth-medium filtrate or other solution to be tested, the difference between the value so obtained and the alkali-centrifuge value of the unexposed fiber being used as an index of *S* activity. Except as otherwise indicated for particular experiments, 250 mg. of well-mixed dewaxed cotton fiber was immersed for a few minutes in distilled water, removed and blotted free of excess water, and then exposed to 25 cc. of filtrate or other solution in a 250-cc. Erlenmeyer flask at 30°C for 1 hr. Unless stated otherwise, *S* activity values

refer to data from undiluted filtrate. The alkali-centrifuge value was determined by a standardized method previously described [12].

Growth of microorganisms was generally carried out in one of three different ways—namely, in shaking or static culture in Erlenmeyer flasks or by a "glass-wick"-culture bottle method (Figure 1). The shaking cultures were incubated with 40 ml. of liquid medium in 250-ml. Erlenmeyer flasks, the growth medium containing some designated carbon source in addition to mineral salts. Reference to "mineral salts" throughout this paper indicates a solution containing the following number of grams per liter of salts: NH_4NO_3, 1.0; KH_2PO_4, 0.90; K_2HPO_4, 0.70; $MgSO_4 \cdot 7H_2O$, 0.75. The static Erlenmeyer incubations were carried out at 30°C in 500-ml. flasks with 1 g. of cotton fiber saturated with 40 ml. of mineral-salts solution. The glass-wick cultures were incubated in 500-ml. French-square bottles, provided with a glass cloth strip as a physical substratum, which was immersed to its upper surface in a liquid medium and which supported upon its surface a 6 in. × 1 in. ravelled strip of unbleached, 8-oz. cotton duck ("Q" duck) (Figure 1). In the preparation of filtrates, the free liquid in the cultures was used, supplemented in the case of fiber-containing cultures by liquid pressed out of the fiber by hand. This liquid was then filtered successively through coarse-, medium-, and fine-porosity fritted-glass crucibles before test.

In tests of the effect of sterile filtrate on breaking strength, a 6 in. × 1½ in. strip of 8-oz. unbleached cotton duck ("Q" duck) was wetted in water, placed in a U-position in the bottom of a large cotton-plugged test tube, and steam-sterilized. About 15 cc. of filtrate, sterilized by the use of a Morton filter, was then added, the cotton plug covered with parafilm paper to prevent evaporation, and the tube placed at a constant temperature of 30°C.

Tests of carboxymethylcellulase activity (similar to Reese's "*Cx*" activity [15]) were carried out by a viscosity method on a 1% solution of carboxymethylcellulose (grade CMC–70M, Hercules Powder Co.) in .05*M* citrate buffer of pH 4.9 at a temperature of 30°C, using Ostwald-Fenske viscometers.

Production of *S* Factor

A pronounced effect of cellulose in the growth medium on the production of *S* factor has been observed. Thus, the use of any of several cellulosic materials in the medium permitted the production of *S* factor by the fungus *Myrothecium verrucaria*, whereas numerous noncellulosic carbon compounds adequate to support good growth did not allow production of the factor in measurable quantity (Table I). In the experiment of Table I, the fungus was grown for 4 days in shaking culture with mineral-salts solution plus various carbon sources, following which filtrates were obtained from the media and tested for *S* activity. The results given in Table I suggested that *S* factor is probably an enzyme or group of enzymes of the cellulase complex. An enzyme whose production is dependent upon the presence of the material on which it acts is referred to as an "adaptive" enzyme [18]. The enzyme cellulase was known to be present in cotton-culture filtrates of the same type as those of Table I; such a filtrate, rendered cell-free by passage through a Morton filter, caused a 27% loss in breaking strength of cotton sheeting exposed to it under sterile conditions for 7 days. Although the activity tests of Table I were run on unbuffered filtrates, there was no indication from the pH values of the filtrates, as shown in the table, which seemed to cast doubt on the adaptive-enzyme interpretation of the data. Rather, it was indicated that the active factor was probably operative over a wide pH range, a conclusion substantiated by later experiments.

The unusually high *S* activity of filtrate from the cotton fiber culture as compared with the activity from other cellulose-containing cultures in Table I may be noted. No thoroughly established explanation for this difference is known, but it is thought probable that noncellulosic growth-stimulative materials in the cotton may be responsible. Yeast extract is known to contain many substances of this nature, and may be noted in the table to have increased the yield of *S* factor from acid-washed filter

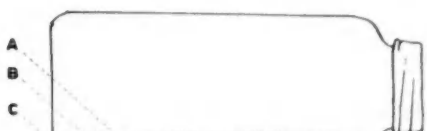

FIG. 1. *Diagram illustrating glass-wick-culture bottle method of incubating cotton fabric with a microbial culture; see also Greathouse, Klemme, and Barker [4].* A—*Cotton fabric strip.* B—*Glass cloth substratum.* C—*Liquid culture medium. Strength and alkali-centrifuge values may be determined on the strip, and S activity on the culture fluid.*

paper. Incorporation of water extracts of cotton fiber in the growth medium in the absence of cellulose failed to result in active filtrates.

Fusarium #102 was incubated in the same manner as the *Myrothecium* in the experiment of Table I, with the essentially similar result that *S*-active filtrates were formed during growth on raw cotton (115) and manila hemp (152), but not on glucose (0), cellobiose (2), starch (−3), pectin (−6), cottonseed oil (0), or gelatin (−1) (the figures in parentheses denote 1-hr. activity values). With these filtrates a buffer was used; the buffer was not entirely effective, the pH's varying between 4.2 and 5.2. *Aspergillus terreus* #45, *A. flavipes* #36, and *Thielavia* #46 also produced active filtrates when grown on cotton fiber, but not when grown on glucose. In a test with *Myrothecium* and with *Fusarium* #102 to determine if active filtrates might be produced in the absence of cellulose if soluble carbohydrate were present but low in concentration, glucose was used as the sole carbon source at a level of 0.2% to 0.02%; no *S* activity was measurable in the filtrates from the cultures.

A similarity between the production of *S* factor and of cellulase is indicated by the data shown in Table II obtained from an experiment with *Clado-*

TABLE I. *S* ACTIVITY * AND pH OF FILTRATES FROM THE GROWTH OF *Myrothecium verrucaria* IN SHAKING CULTURE ON A MINERAL SALTS SOLUTION CONTAINING CARBON FROM VARIOUS SOURCES †

Carbon source in medium	*S* activity of filtrate 1 hr.	*S* activity of filtrate 4 hrs.	pH of filtrate
Cellulosic C sources			
Bacterial cellulose‡	22	74	6.5
Carboxymethylcellulose§	59	110	6.9
Cellophane	92	122	5.8
Corn stalk, ground	104	142	5.4
Cuprammonium rayon‖	74	121	5.5
Filter paper (acid-washed)	43	84	5.1
Filter paper (acid-washed) plus .03% yeast extract	68	108	5.2
Filter paper (qualitative)	62	108	5.0
Flax fiber	81	135	5.0
Manila hemp	99	156	5.3
Raw cotton	148	161	5.3
Wood shavings	105	153	6.2
Noncellulosic C sources			
Asparagine	2	1	8.4
Cellobiose	−2	0	5.8
Cotton extract**	−4	−5	7.8
Cottonseed oil	6	9	4.6
Gelatine	5	1	8.4
Glucose	−4	−6	6.4
Glucose plus cotton extract	−6	0	8.0
Glycerine	2	8	5.8
Lactose	−7	−5	5.3
Malic acid	−1	−1	6.4
Pectin (Eastman Kodak Co., tech.)	0	8	7.1
Peptone	−9	−12	5.2††
Starch	9	0	4.8
Sucrose	10	10	5.5
Wool (autoclaved 2 hrs.)	1	−6	7.5

* In terms of change in alkali-centrifuge values of a test fiber as a result of exposure to the filtrate. This experiment was conducted at an early period in our experience with the alkali-centrifuge test, and the results consequently are slightly less accurate than in later experiments.

† In all cases moderate to heavy growth occurred, except for only slight visible growth on the wood shavings.

‡ Membrane from growth of *Acetobacter xylinum*, purified by washing successively with dilute NaOH, dilute acetic acid, and water.

§ "Carbose I," from Wyandotte Chemical Co., 250 mg. of which was autoclaved at 15 lbs. for 15 min. in the mineral-salts medium; the undissolved residue was removed before inoculation.

‖ Water-washed to remove copper.

** Made by kneading 50 g. of raw cotton at room temperature with 500 cc. of water. In the cotton-extract tests the salts were simply added to this medium rather than to distilled water.

†† Filtrate was buffered.

sporium #113 and *Fusarium* #102 incubated with cotton fabric strips in the glass-wick-mineral-salts system of Figure 1. When only mineral salts were used in the liquid culture medium, rapid decreases in strength of the strip took place, with concomitant increases in the alkali-centrifuge value of the strip and in the *S* activity of the culture fluid, as measured in the customary fashion (Table II). When 1% glucose was added to the culture fluid at the beginning of the incubation, however, all three of these changes were retarded simultaneously. The fungus presumably utilized the glucose first and preferentially in respect to the cellulose of the strip, and produced no *S* factor and caused no loss in strength of the strip until the glucose had been largely depleted or exhausted. The filtrates were buffered at pH 4.7 with .05*M* citrate buffer. The action of the glucose in the experiment of Table II was not merely one of inhibition of action of *S* factor, as shown by the fact that 1% glucose added directly to an active filtrate exerted no effect on its *S* activity.

The ability to produce *S* factor was found to be a property of *Myrothecium verrucaria* #1334.2 which is at least moderately stable in the sense that it is not lost upon repeated transfer of the fungus on a medium containing only glucose as a carbon source. Mass inoculations were made upon glucose-mineral-salts agar (1% glucose) twelve times in succession, after which twelve single-spore isolations were made on the same glucose-mineral-salts agar from the twelfth mass culture. Upon their first transfer to a cotton mat and incubation for a week in the usual manner, the twelve isolates produced filtrates with *S* activities of 120, 126, 131, 132, 137, 132, 126, 133, 136, 130, 127, and 127. When tested under the same conditions, the original mass isolate, which had been maintained and repeatedly transferred on filter paper for a period of several years, yielded a value of 131. The behavior of *M. verrucaria* with respect to *S* factor and cellulose is thus obviously "adaptive" in the strict sense [18], and under the described conditions is little if at all dependent upon genetic mutations and substrate-induced "educative" changes in the proportions of mutant types within a culture.

A few generalizations of a practical nature with respect to production of *S* factor may be offered for the use of individuals interested in experiments with it. In the static cotton-mat incubation procedure with *M. verrucaria*, activity regularly exceeds 100 and often reaches 150 when the filtrate is produced during 1-week growth by this method. The exact level of activity depends in some unknown way upon the particular sample of cotton used for the mat. When a constant source of cotton is used for the incubation mats, the activity is quite uniform from one flask to the next and from one incubation to the next. Thus, *S* values of 151, 146, 148, 150, and 153 were obtained, for example, for undiluted filtrates from five separate incubations at different times on cotton mats taken as subsamples from a single large source of fiber. The yield of *S* factor by the cotton-mat procedure is somewhat lower from older cultures in contrast to that from younger cultures, mats of 1, 2, 3, 4, 5, and 6 weeks yielding *S* values of 151, 136, 117, 113, 116, and 107, respectively. This result, of course, does not necessarily indicate progressive destruction or inactivation of the factor, which may simply be more tenaciously retained by the older mats. The pH's of these filtrates were 6.2, 7.1, 7.1, 7.1, 7.0, and 7.0, respectively; pH may have exerted a contributory effect in lowering the activity of the filtrates from the older cultures, since lowered activity has been observed in the vicinity of pH 7. Filtrates are perfectly clear and faintly yellowish in color.

TABLE II. RETARDING EFFECT OF 1% GLUCOSE IN THE CULTURE MEDIUM ON CHANGE IN PROPERTIES OF THE INCUBATED STRIP AND ON PRODUCTION OF *S* FACTOR IN THE LIQUID CULTURE MEDIUM *

Fungus	Culture medium	Properties of the incubated strip		*S* activity of the liquid culture medium
		Strength change (%)	Alkali-centrifuge value	
Cladosporium #113	Mineral salts	−18	357	139
Cladosporium #113	Mineral salts plus glucose	−1	296	76
Fusarium #102	Mineral salts	−33	370	148
Fusarium #102	Mineral salts plus glucose	+1	304	41

* Four-day incubation with the glass-wick-culture bottle method (Figure 1).

Production of *S* factor as measured by the usual *S* test on cotton-culture filtrates is not necessarily proportional to the change in alkali-centrifuge value of the fiber used as the growth substrate for the incubation. The explanation for this situation is not known. It might result from a difference in retention of *S* factor by the incubated fiber or fungus mycelium, from some difference in stability or other property of the enzyme as produced by different fungi, or even from some difference in nonenzymatic constituents of the filtrate which influence *S* activity. As an illustration of the phenomenon, the behavior of *Chaetomium globosum* #1042.4 may be contrasted with that of *M. verrucaria* (Table I). When *C. globosum* was grown in shaking mineral-salts solution with cotton fiber for periods of 1, 2, 3, 4, and 7 days, alkali-centrifuge values of the incubated fiber for these periods were 216, 346, 365, 359, and 343, respectively, whereas *S* activities of the filtrates from the same cultures were only 7, 11, 19, 25, and 17, respectively.

S factor was present in relatively low but significant amounts in enzyme preparations of unknown method of production marketed under the designations "cellulase" and "hemicellulase" (Bios Laboratories). In a 4-hr. test with 10 mg. of enzyme preparation, 10 ml. of solution (.05*M* citrate buffer, pH 4.5), and 100 mg. fiber, *S* activities of 50 and 67 were obtained for the two preparations, respectively. Various noncellulolytic enzyme preparations yielded negative results—namely, pepsin, trypsin, takadiastase, and "Clarase." Several nonmicrobial sources have been tested, all with negative results. These sources included press-juice preparations from fruits of the peach, watermelon, tomato, banana, and cotton (unopened bolls) and "milk" from a coconut.

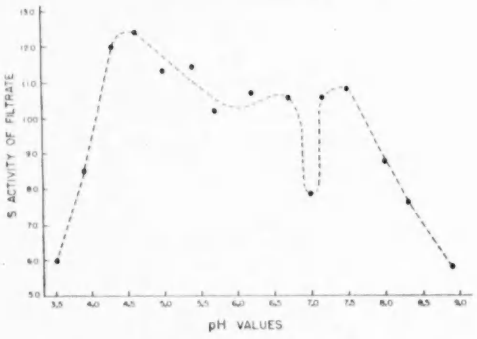

FIG. 2. *Influence of pH of* Myrothecium *filtrate on its* S *activity. Adjustment of pH with an ammonia-citrate buffer, .05*M *in citrate in the test solution.*

Properties of *S* Factor

S factor was found to be active over a wide range in pH. Using filtrate buffered with citric acid and ammonia at a final citrate concentration of 0.05*M*, the pH-activity curve shown in Figure 2 was obtained. The question of possible specific ionic effects and other phenomena which might modify pH-activity curves has not been critically examined. However, it has been noted that certain neutral salts generally not strongly inhibitory to enzymes depress *S* activity in rather low concentrations. In an experiment with filtrate diluted 25 times with water, the control-sample activity of 73 was lowered to 34, 55, 53, and 49 as a result of the addition of KCl, NaCl, $CaCl_2$, and $MgSO_4$, respectively, to a final concentration of only .01*M*.

The rate of action of *S* factor on cotton fiber and the rate of its uptake from solution by the fiber were followed by placing uniform cotton samples in several aliquots of filtrate, removing the samples from the different aliquots after successively increasing periods of time, and determining their alkali-centrifuge values, and by also measuring the residual *S* activity of the same aliquots in the usual manner after the first set of samples had been removed. The first or variable-time exposure involved 300-mg. dewaxed samples mechanically shaken with 30 cc. of filtrate diluted 15 × with water, leaving more than enough volume of filtrate for the standard

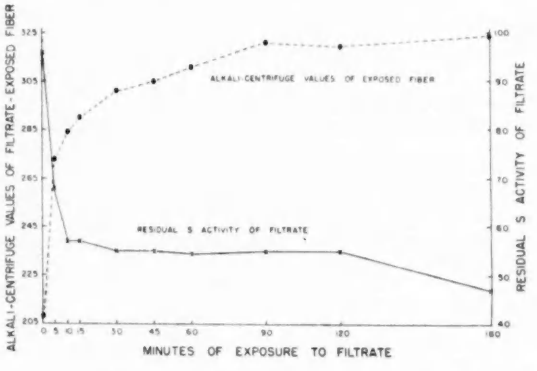
ALKALI-CENTRIFUGE VALUES OF FILTRATE-EXPOSED FIBER
ALKALI-CENTRIFUGE VALUES OF EXPOSED FIBER
RESIDUAL S ACTIVITY OF FILTRATE
RESIDUAL S ACTIVITY OF FILTRATE
MINUTES OF EXPOSURE TO FILTRATE

FIG. 3. *Rate of change in alkali-centrifuge value of cotton fiber under the influence of 15 ×-diluted* Myrothecium *filtrate and rate of uptake of* S *factor by the fiber from this diluted filtrate, the latter measured in terms of residual* S *activity of filtrate after exposure of fiber to it.*

25-cc. activity assay. As may be seen from Figure 3, an increase of 65 in alkali-centrifuge values occurred during the first 5 min. of exposure, with an additional increase of 48 to a near-maximum value at 90-min. exposure. A major part of the total removal of *S* factor from solution occurred within 10 min., and uptake thereafter progressed much more slowly (Figure 3). These results suggest that uptake consists largely of adsorption of *S* on the outer surface of the fiber. In spite of the mechanical shaking, the rate of uptake in this experiment might very well have been limited by the time required to obtain thorough mixing of the filtrate throughout the fiber mass, and under conditions of more nearly ideal or instantaneous mixing the large uptake observed in the first 10 min. in the experiment of Figure 3 might have been essentially instantaneous.

Although the rate of change in alkali-centrifuge values of cotton fiber exposed to *S*-active *Myrothecium* filtrates is very rapid, loss in strength occurs much more slowly (Table III).

Myrothecium filtrates were found to be at least moderately stable in *S* activity under certain investigated conditions. Filtrates sterilized by passage through a Morton filter and stored under sterile conditions in cotton-plugged flasks at 20°C for 3 weeks showed only a slow loss in activity, *S* values of 114, 103, 104, and 92 being obtained at the 0-, 1-, 2-, and 3-week periods of storage, respectively.

Drying of filtrates may be accomplished at moderate temperature with little if any destructive action on *S* activity, and dried films show essentially the same *S* activity as they exhibited originally when restored to volume with water after a month in a dry condition (Table IV). In this experiment dilutions of the filtrate were dried in Petri dishes in a forced-draft oven and restored to volume with water before testing. The fact that *S* factor may retain its activity over long periods of storage in a dry state was also noted as an incidental result of experiments with a dry commercial preparation marketed under the name "Pectinol 100 D," but known to its producers (Rohm & Haas) and others [21] to contain significant amounts of cellulase. A sample of this preparation showed high *S* activity after 8 mos. storage in our laboratory. Its cellulolytic activity was apparent from the fact that a water extract of the preparation (100 ml. of water to 25 g. of the Pectinol), filtered through a Morton filter and kept in contact with unbleached 8-oz. cotton duck under sterile conditions for 2 weeks, brought about a strength reduction of 33%. *Myrothecium* filtrates also retain their activity if simply frozen and stored in a deep-freeze refrigerator.

S factor may be precipitated from *Myrothecium* filtrates with acetone. In an experiment, acetone was mixed with *Myrothecium* filtrate in proportions of 50%, 65%, and 80% of the total volume of the mixture. After 1 hr. at about 5°C, the mixtures were centrifuged, and the precipitates and supernatant liquids were separated and reduced to dryness at 40°C in a circulating oven. Water was then added to both dried precipitate and dried supernatant to the volume of the original filtrate, and a test of *S* activity was run at a citrate-buffered pH of 4.8. The supernatant samples corresponding to the 50%, 65%, and 80% acetone exhibited *S* values of 62, 14, and 3, respectively, while the pre-

TABLE III. EFFECT OF STERILE *Myrothecium* FILTRATE ON ALKALI-CENTRIFUGE VALUES AND STRENGTH OF 8-OZ. UNBLEACHED COTTON DUCK

Period of exposure	Change in alkali-centrifuge values*	Change in strength† (%)
4 hrs.	+105	+2
7 days	+138	−33
14 days	+150	−39
21 days	+154	−45

* Control strips exposed to sterile mineral-salts solution exhibited changes of −4, +3, −3, and 0.

† Control strips exposed to sterile mineral-salts solution exhibited changes of +1%, +3%, −3%, and +7%.

TABLE IV. EFFECT OF DRYING AT 40°C AND OF THE SAME FOLLOWED BY 4-WEEK STORAGE AT ROOM TEMPERATURE IN DRY CONDITION ON *S* ACTIVITY OF A *Myrothecium* FILTRATE

	S activity of:		
Dilution	Original filtrate	Filtrate dried and restored to volume	Filtrate dried, stored dry 4 weeks, and restored to volume
5×	106	105	97
10×	91	90	85
25×	68	70	61
50×	54	53	58
100×	38	34	38

cipitate samples showed activities of 84, 100, and 89, respectively.

Further light on the nature of *S* factor is provided by the finding that the factor undergoes progressive inactivation when subjected to the action of the crystalline enzyme pepsin. In experiments, 2 mg. of crystalline pepsin (Bios Laboratories) was added to 25 ml. of 10×-diluted filtrate previously adjusted to a pH of 3.0. After different periods of time, the pH of the filtrate was readjusted to 4.5, and 250-mg. samples of dewaxed cotton were added and incubated for the usual 1-hr. assay period. The *S* activity values for the filtrates exposed to the pepsin for 1, 2, 3, and 4 hrs. were 54, 32, 27, and 17, while control filtrates exposed for equal time periods to the pH of 3.0 in the absence of pepsin had activities of 85, 77, 76, and 59, respectively.

It was shown previously that *Myrothecium S* factor may be destroyed by heating [12]. However, the heating procedure used in this earlier experiment (autoclaving for 30 min. at 15 lbs. steam pressure) was considered drastic, and it was thought that some further insight into the nature of *S* factor might be obtained by less severe heat-inactivation procedures.

When a solution of known *S* activity was distributed in equal amounts into individual flasks and these flasks were subjected to a ½-hr. heat treatment at different temperatures, the *S* activity remaining, as measured at 30°C in the usual manner shortly after heating, did not exhibit a uniformly decreasing level according to the temperature of the previous heating (Table V). Although heat inactivation began at relatively low temperatures, around 55°C, it was not complete after ½ hr. heating at even 100°C. The filtrate diluted with water (a 1:5 dilution) was distinctly more resistant to complete inactivation than the filtrate equally diluted to contain a final concentration of .05*M* citrate buffer, pH 4.5. A visibly greater degree of cloudiness developed in the filtrate heated at pH 4.5. The resistance of *Myrothecium* filtrate to complete *S* inactivation by heat was also indicated by an experiment with heating periods of up to 6 hrs. at 55°C (Figure 4).

TABLE V. EFFECT OF HEATING FOR ½ HR. AT DIFFERENT TEMPERATURES ON SUBSEQUENT *S* ACTIVITY OF *Myrothecium* FILTRATE AT 30°C

Temperature of heating (°C)	*S* activity of filtrate: Heated and tested at 5× water dilution*	Heated at 5× water dilution, tested at pH 4.5†	Heated and tested at pH 4.5†
30‡	116	108	103
40	131	109	114
45	126	107	98
50	134	111	103
55	100	96	66
60	78	83	57
65	61	83	65
70	67	77	40
75	52	63	23
80	67	62	29
85	61	60	28
90	59	60	28
95	58	55	22
100	46	45	16

* Alkali-swollen fiber widths for fiber treated at a 100:1 ratio with filtrate previously heated at 30° (unheated control), 55°, 65°, 75°, 85°, and 95°C exceeded the untreated control width (26.2μ) by 8.7, 7.4, 5.7, 4.7, and 4.7μ, respectively, thus confirming the heat tolerance of *S* factor as measured by the centrifuge method.

† Citrate buffer of final concentration .05*M*.

‡ Unheated control.

Since the filtrate of Table V and Figure 4 was produced on cotton mats and since cotton fiber is not made up entirely of cellulose, it was thought that this filtrate might possibly contain two adaptive *S*-active enzymes, one more thermostable than the other, and that only one might be produced during growth on filter paper. Accordingly, *Myrothecium* was grown on filter paper by the shaking-culture method, and a heat-inactivation test of the filtrate was carried out. A filtrate diluted 5× with water and having an *S* activity of 84 at this dilution was heated and tested; it yielded *S* activities of 62, 44, 35, 30, and 29 after heating for ½ hr. at 55°, 65°,

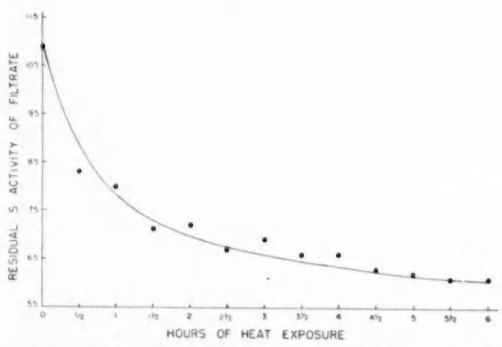

FIG. 4. *Residual S activity of a* Myrothecium *filtrate as tested at 30°C after heating for different time periods at 55°C.*

75°, 85°, and 95°C, respectively, thus providing no indication of elimination of either a heat-sensitive or a heat-resistant fraction of *S* as a result of growing the fungus on filter paper.

The degree of heat tolerance manifested by *S* factor was rather surprising. An even lesser degree of heat tolerance exhibited by "hydroxyethylcellulase" in the experiments of Ziese [23] prompted Siu ([17], p. 273) in reviewing the work to doubt the enzymatic nature of the phenomena observed by Ziese. The possibility was considered that the heat tolerance of *S* factor might be an artifact of some sort specifically associated with the *S*-activity test. In checking this possibility it was noted that heat tolerance was also clearly apparent when the results were measured in terms of alkali-swollen fiber width (Table V). Further, it was observed that *Myrothecium* filtrates also exhibit a very high degree of resistance toward complete heat inactivation when tested for action in lowering the viscosity of carboxymethylcellulose—that is, by a method essentially similar to that used by Levinson and Reese [9] to measure a component of the cellulase complex designated as "*Cx*." Data on this are shown in Table VI. It is not concluded from these data that carboxymethylcellulase is necessarily identical with or different from *S* factor, but only that the high heat tolerance of *S* factor is probably not an artifact associated with the method of measuring its activity.

TABLE VI. CARBOXYMETHYLCELLULASE ACTIVITY* OF *Myrothecium*-COTTON-MAT FILTRATE HEATED PRIOR TO TEST

Temperature of heating (°C)	Activity of filtrate heated for: ½ hr.	1 hr.	2 hrs.	3 hrs.
55	126	125	122	121
75	37	36	33	—
85	39	36	27	15
95	36	26	10	3

* Activity was measured as reduction in flow time (sec.) of 10 cc. of 1% carboxymethylcellulose resulting from the action of 0.1 ml. of filtrate for 30 min. at 30°C. Flow time with no filtrate, 201 sec.; activity of unheated filtrate, 130 sec.

The metabolism of the fungus cell as a whole is obviously not adapted to high temperatures. Rather, this fungus is similar to many other fungi in its temperature requirements for growth. It grows best at a temperature of about 30°C, and probably will not maintain continued growth at any temperature much above 35°C ([17], p. 189).

Although complete *S* inactivation occurred only at high temperatures, a major loss in activity also occurred at moderate temperatures (Table V). It was thought that this latter partial inactivation might result merely from adsorption of *S* on nonenzymatic protein of the filtrate precipitated by the heating. To test this possibility, the activity of an unheated filtrate diluted with an autoclaved filtrate was tested in comparison with that of the same unheated filtrate diluted with water. At 2×, 5×, 10×, and 25× dilutions, the normal filtrate diluted with autoclaved filtrate exhibited *S* activities of 127, 111, 99, and 70 in comparison with the very closely similar values of 123, 121, 102, and 64 for the water-diluted filtrate, the experiment thus failing to disclose inactivation of the expected type.

The effect of heat *during a period of enzyme action* on the amount of action which occurs has been observed by workers with other enzymes to be dependent upon the length of the assay period and the conditions of the test. The net effect at above room temperature may be the result of two counteracting effects—namely, the increase in activity of individual enzymes molecules and the increase in the rate of their destruction. Data obtained with cotton-mat-*Myrothecium* filtrates acting for 1 hr. on dewaxed cotton in the usual *S* assay showed that the temperature range suitable for rapid *S* activity by these filtrates (Table VII) is higher than that for many other enzymes.

One of the principal means available for characterizing an enzyme is to determine the increase or decrease in its activity which results when various known materials are added to the enzyme system. Inhibition of enzyme action by sodium azide, for example, is characteristic of heavy-metal-containing

TABLE VII. EFFECT OF TEMPERATURE DURING THE ASSAY PERIOD ON THE ACTIVITY OF *S* FACTOR IN *Myrothecium*-COTTON-MAT FILTRATES

Experiment	Dilution (water)	*S* activity at temperatures (°C) of: 5	10	15	20	25	30	35	40	45	50	55	60
A	25×	43	49	51	62	66	68	83	86	107			
B	15×	—	—	—	—	—	102	—	109	100	95	95	64

enzymes, and is observed with various oxidases. Since *S* factor exhibits complete insensitivity to sodium azide (Table VIII), it may be concluded that it is probably not a heavy-metal-containing enzyme, or at least not an enzyme in which substrate reaction with the heavy-metal component of the enzyme molecule is a feature of its action. Reaction with mercury is characteristic of proteins generally (Table VIII). The peculiar phenomenon of resistance of *S* factor to complete inactivation by $CuSO_4$ may be noted as characteristic.

Discussion

One question of interest with regard to *S* factor seems to merit discussion even though it remains only partially answered. This question concerns the problem of whether *S*-active enzymes are entirely cellulolytic or whether some noncellulolytic enzymes may also exhibit *S* activity. This question is made complex by the uncertainty and incompleteness of available information relating to the nature of the primary wall of the cotton fiber [5, 20], on which *S* is believed to act. It has been proposed that not only cellulosic but possibly pectic materials also may contribute to the structural strength of the primary wall [6]. Some workers believe that the naturally occurring protopectin of plant cell walls consists of cellulose-pectin molecules, while others question this view [7].

It was thought that some light might be thrown on the possibility of enzymatic noncellulolytic *S* activity if noncellulolytic microorganisms could be found which would bring about increases in the alkali-centrifuge values of cotton fiber. In this connection, it was observed that certain organisms previously regarded as incapable of cellulolytic action may bring about increases in the alkali-centrifuge values of cotton fiber when grown in its presence. The fungi of the order Mucorales have generally been considered noncellulolytic [11, 16, 17, 22]. When five isolates of this order—namely, *Circinella sydowi* 9023, *Cunninghamella* 8985, *Mucor hiemalis* 8977a, *Mortierella alpina* 8979, and *Zygorhynchus* 7935—were grown in shaking culture for 5 days in a mineral salts-.2% glucose medium also containing 250 mg. of raw cotton, the alkali-centrifuge values of the thus-incubated fiber increased to 318, 271, 310, 298, and 304, respectively, with a concomitant increase of microscopically measured swollen-fiber width to 34.1, 28.1, 34.3, 32.1, and 33.6 μ. An uninoculated control sample incubated under sterile conditions yielded an alkali-centrifuge value of 222 and a swollen-fiber width of 26.6 μ, these values being similar to those of unincubated fiber. Filtrate from one of the above cultures, that of the *M. hiemalis*, was tested under sterile conditions on undamaged fiber for a week; it raised the alkali-centrifuge value from 218 to 254, thus demonstrating low but significant *S* activity. When the same *Mucor hiemalis* was inoculated on unbleached cotton duck in the glass-wick procedure (Figure 1) in the presence of mineral salts and .2% glucose, it caused no loss in strength, but an increase in the alkali-centrifuge value of the strip from 230 to 275 in 7 days. The usual 1-hr. assay did not detect *S* activity in the culture liquid.

Although one might be inclined to believe from the data of the preceding paragraph that some noncellulolytic enzymes may be *S*-active, this conclusion obviously rests on a premise which is subject to question—namely, that the fungi of the Mucorales are really entirely incapable of attacking cellulose. It could be argued logically that the alkali-centrifuge test, as applied to this incubated fiber, is simply a very much more sensitive test of cellulolytic activity than has been applied previously to the members of the Mucorales, and thus detects a low level of action not observed by other methods. While certain microorganisms are obviously cellulolytic, as shown by their rapid production of strength loss in cotton and active growth on filter paper [11, 16, 17], the conclusion that a fungus is entirely incapable of cellulolytic action is not so easily proven valid.

TABLE VIII. EFFECT OF ENZYME INHIBITORS ON THE ACTIVITY OF *S* FACTOR IN *Myrothecium* FILTRATES

Inhibitor	Change in *S* activity (%) with inhibitor at a molarity of:						
	10^{-5}	3×10^{-5}	10^{-4}	3×10^{-4}	10^{-3}	3×10^{-3}	10^{-2}
NaN_3	−1	0	−5	0	+2	0	+5
$CuSO_4$	+14	+3	−28	−49	−64	−64	−67
$AgNO_3$	−25	−28	−30	−52	−66	−75	−83
$HgCl_2$	−10	−51	−98	−100	−98	−100	−98

It was thought possible that some organism might be found which would produce large amounts of protopectinase but still exert no *S* activity on cotton fiber. Two bacteria which exhibit high protopectinase activity were available to us, *Erwinia carotovora* and *E. atroseptica*. These organisms cause the well-known bacterial soft rot of vegetables, and their activity in bringing about separation of cells in such tissues is widely described as a manifestation of protopectinase action on the pectic lamellae which occur between these cells. When these bacteria were grown on Irish potato slices, they produced the expected semiliquid condition characteristic of bacterial soft rot. This liquid, however, manifested distinct *S* activity on cotton fiber. Further, when tested on carboxymethylcellulose at a 1:100 dilution, it also caused a distinct progressive decrease in the viscosity of this material, indicating the presence of an enzyme of the cellulase complex as well as protopectinase. It was thought of interest to check *Myrothecium*-cotton-mat filtrate for activity in the protopectinase test on carrot discs. When carrot discs were left in Morton-filter-sterilized *Myrothecium* filtrate under sterile conditions for a week, a very major amount of disintegration of the carrot tissue occurred, the remaining material consisting almost entirely of the spiral and pitted secondary thickenings of the xylem vessels. Cell separation had obviously occurred. In view of the possibility that the middle lamellae may be composed of a cellulose-pectin material, one is led to wonder if the "protopectinase" action in this case may not actually have been caused by cellulase.

Although the high heat tolerance here reported for *S* factor in *Myrothecium* filtrates may seem unusual, it should be noted that high or relatively high heat tolerance has also been noted by others with certain other enzymes—notably, amylase [1], hyaluronidase [14], trypsin, ribonuclease [8], and a pectolytic factor from tomatoes [13]. No inference is intended to the effect that *S* factor in isolated condition would or would not necessarily exhibit such high tolerance, it being recognized that nonenzymatic materials accompanying *S* factor in *Myrothecium* filtrates might greatly influence this property.

It was observed as a curious experimental fact that raw cotton, with its natural coating of wax, exhibited almost or possibly quite as rapid a change in alkali-centrifuge values under the influence of *Myrothecium* filtrates as did dewaxed fiber. Further, the amount of removal of *S* factor from solution by raw cotton was almost the same as for the same fiber dewaxed. Data on these points have not been shown, but were obtained by an experiment very similar to the one whose results are shown in Figure 3. It was thought that the filtrate might be removing the wax by enzymatic action. However, after filtrate action for 2 hrs., a sample which had increased to 334 in alkali-centrifuge value yielded .57% wax by the Conrad method [3], as compared with .52% for the original fiber. The wax from the filtrate-treated sample had a melting point somewhat lower than that from the original fiber. It seems possible that large numbers of cracks in the waxy layer may allow penetration of the enzyme without removal of the wax.

Summary

Filtrates from certain microbial growth media have been found active in increasing the degree of alkali-swelling of cotton fibers. Numerous experiments have been described which relate to the production and properties of the active material, here termed "*S* factor."

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(*Manuscript received June 11, 1953.*)

Hemicellulose in the Viscose Rayon Process
A Chromatographic Investigation

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Introduction and Aim of the Investigation

In the literature there is some vagueness concerning the definition of "hemicellulose." However, all the definitions proposed agree that the term "hemicellulose" refers to those cell-wall polysaccharides in a cellulosic material which can be extracted by aqueous alkali.* In raw materials like wood, straw, etc., the hemicellulose consists of (*a*) polyuronides, which yield uronic acids and monomer sugars on hydrolysis, and (*b*) the less easily extractable cellulosans, which on hydrolysis give hexoses and pentoses, and only traces of uronic acids. The cellulosan of gymnosperms contains glucosan, mannan, and some xylan, and that of angiosperms, glucosan and xylan.

The hemicellulose of the pulps used by the viscose rayon industry consists almost entirely of cellulosans, the polyuronides being removed in the pulping process. According to the type of wood used in the preparation of the pulp, mannan or xylan may be expected to be present in the latter, together with glucosan. Moreover, small amounts of galactose, arabinose, and sometimes fructose have been found in the hydrolyzed cellulosan portion of hemicelluloses.

In the manufacturing process of viscose rayon most of the hemicellulose present in the pulp is dissolved in the 18% NaOH used in the steeping operation. Actually, it is customary in this industry to

* *cf.*, A. G. Norman, in E. Ott's "Cellulose and Cellulose Derivatives," 2nd ed., New York, Interscience Publishers, Inc., 1946, p. 430.

define "hemicellulose" as that part of the pulp which is soluble in the steeping liquor. The extent to which the hemicellulose is removed on steeping is rather critical and must be kept within narrow limits, because the hemicellulose content of the alkali cellulose obtained after draining and pressing exerts a noticeable influence on the liability of the rayon to show "milkiness," on the mechanical properties of the yarn, on the speed of crumb aging and of viscose ripening, etc.

In view of the sensitivity of the technical process as to the "hemicellulose policy" followed in the rayon factory, it is worth while to obtain information regarding the percentage and the composition of the hemicellulose present in the lye which is drained or pressed from the alkali cellulose after steeping, in the unaged and aged alkali cellulose, in the spinning and aftertreatment baths used, and in the final products. Although a possible way to carry out such an investigation would be the analysis of the various corresponding acid hydrolyzates by the classic methods of sugar chemistry, it seemed to us that a much simpler means to gain some semiquantitative insight into this matter would be provided by the modern method of partition chromatography.

Chromatography of Monosaccharides

Partition chromatography on filter paper has proved to be a useful tool in the qualitative and quantitative analysis of sugar mixtures. A recent review of the development of this method was given by Hirst and Jones.* Numerous papers dealing with the subject appeared subsequently in the literature.

In most of the investigations published the conventional method, using strips of filter paper, was followed. However, after a few preliminary experiments it became clear that in the present study the use of circular chromatograms would have certain advantages.†

In the center of a disc of filter paper ‡ (diameter, 24 cm.) a point is made with a pencil. A known quantity of the sugar mixture is put on the paper with the aid of a micropipet by placing the tip of the pipet on the black point and allowing the given quantity to be sucked slowly into the paper (0.1 ml. of a 1% solution). The filter disc is then put into a drying oven for a few minutes in order to allow the wet stain to dry. A small hole is then punched in the paper by means of a dissecting needle, exactly at the place of the black point.

A glass dish partly filled with water-saturated *n*-butanol is placed in a desiccator (inner diameter, 20 cm.). A small cone of filter paper with a pin projecting through its top stands in the dish. The disc of filter paper is laid on the rim of the desiccator in such a way that the pin of the cone sticks through the hole in the center of the disc. Care should be taken that the top of the cone is in contact with the center of the disc. Such contact is ensured by loading the central part of the filter-paper disc with a glass ring of about 5 cm. diameter. Under and on top of the filter-paper disc, rings of filter paper lie on the desiccator rim. The desiccator is closed by means of a lid. (See Figure 1.) The development of the chromatogram is carried out at 20°C. On developing, the various sugars form a system of rather sharp concentric rings in the disc, which displace themselves at characteristic speeds.

After developing, the disc is dried in the air and the rings are made visible by spraying with a solution of 1.82 g. of benzidine and 1.65 g. of trichloroacetic acid in 100 ml. of ethanol and heating at 110°C for 10 min. With this reagent the pentoses give a deep violet color, whereas the hexose rings become yellowish brown.

The benzidine trichloracetic acid reagent has a certain disadvantage in that it is only applicable to aldoses. In the present case this does not have serious consequences because only negligible amounts of ketoses are present in the pulp hydrolyzates.

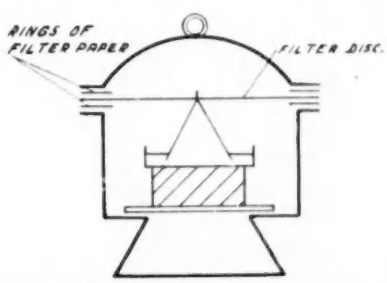


FIG. 1. *Desiccator with filter-paper cone and disc.*

* E. L. Hirst and J. K. N. Jones, *Discussions Faraday Soc.* **7**, 268 (1949).

† The work described here was carried out in 1950 and 1951; our method was developed independently of that by S. Rosebeek, *Chem. Weekblad.* **46**, 813 (1950), and it has some advantages over the latter. Earlier work in this field was published by Goppelsroeder, F., *Kolloid Z.* **4**, 23, 94, 191, 236, 312 (1909), and more recently by Rutter, L., *Nature* **161**, 435 (1948).

‡ Whatman No. 1 or Schleicher and Schüll No. 589² was used.

The method of circular chromatography was chosen because it permits a more rapid and sharper separation than does the linear method. A disadvantage of the circular method is that filter-paper discs of a rather large diameter would be required for the determination of R_F values. We did not possess sufficiently large desiccators and filter-paper discs and therefore had to resort to the method of using rings of filter paper, as mentioned above. In this way we succeeded in obtaining well-separated rings of sufficiently large diameter. However, since characterization of the rings by their R_F values is not possible with this method, it was necessary to identify them by their relative positions. In order to render semiquantitative work possible by estimation of color intensities, it was necessary to obtain chromatograms in which the corresponding rings had about the same diameter.

In experiments with pure sugars the following values were found for the radii * of the rings after 20-hrs. developing: xylose, 7.1 cm.; arabinose, 6.4 cm.; mannose, 6.3 cm.; glucose, 5.5 cm.; galactose, 5.1 cm.

With regular hydrolyzates we always tried to obtain a glucose ring with a radius of 5.5 cm. (glucose is almost always present in the hydrolyzate).

The arabinose and mannose rings lie very close together; for complete separation, much longer developing times than 20 hrs. are required. However, since the two sugars give rings of different colors, identification is possible even when separation is incomplete; in such a case, when both sugars are present, the outer edge of the ring will be violet and the inner one brown.

Disaccharides, trisaccharides, and higher sugars give rings with diameters smaller than those of the monosaccharides.

Chromatography of Hydrolyzates

The hydrolyzates to be analyzed are obtained as solutions in saturated (41%) hydrochloric acid. Before making the chromatogram, the acid must be evaporated and the mixture must be freed from inorganic substances as much as possible.

A typical example of a complete analysis—that of a hemicellulose containing lye—is given below.

A quantity of lye, in which about 250 mg. of hemicellulose are present, is weighed. This lye is neutralized with concentrated HCl while cooling. The solution is further cooled to 0°C, and gaseous HCl is passed through it until saturation is reached. The sodium chloride present precipitates almost completely, after which filtration follows through a glass filter; the salt is washed twice with 25 ml. of 41% HCl. The filtrate and the washing liquor are transferred to a 250-ml. measuring flask, which is filled up to the mark with 41% HCl. The measuring flask is left at 20°C for 3 days. After this period 100 ml. is concentrated in a round-bottomed flask under vacuum to a volume of 1–2 ml. During this procedure the temperature of the hydrolyzate is not allowed to exceed 30°C. The evaporated residue is diluted with 10 ml. of water, and is then passed through an anion-cation exchanger to liberate it from acid and salt. Washing with 100 ml. of distilled water follows. In another round-bottomed flask the solution plus the collected washing liquor are evaporated in vacuum until completely dry. The residue is dissolved in 10 ml. of water in which 0.1% of phenol is present as an antiseptic. A chromatogram of this solution is made as described above.

In order to arrive at a semiquantitative estimation of the amounts of the various sugars present in the hydrolyzate, the chromatogram must be compared with chromatograms of sugar solutions of known concentration. Such comparison chromatograms must be prepared anew for every hemicellulose analysis, because the colors fade. It is advisable to have the chromatograms examined independently by two persons.

Apart from the possible error in the estimation of the color intensities, the following factors may affect the accuracy of the method: (*a*) incomplete hydrolysis; (*b*) occurrence of secondary reactions during the hydrolysis. However, for semiquantitative work the method seems to be adequate; for example, in the hydrolysis of pure (linter) cellulose, more than 90% of the theoretical amount of glucose was found.

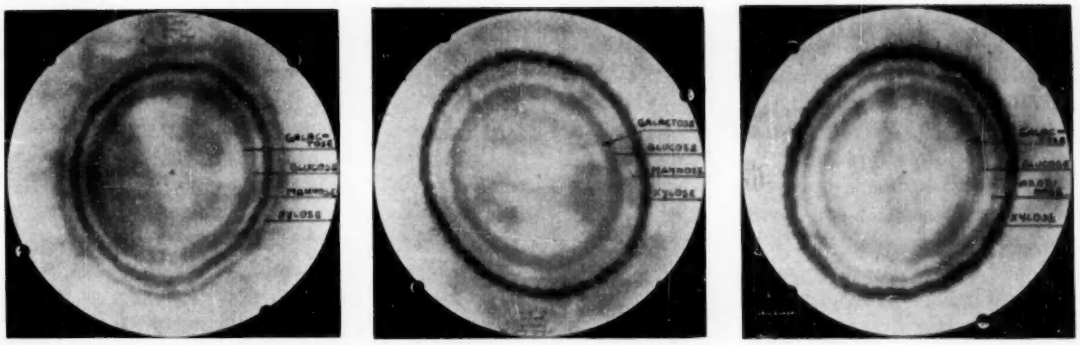
It should be mentioned that all of the analyses described in the present paper were carried out in duplicate.

Experimental Results

Extracts of Raw Vegetable Materials and of Pulp

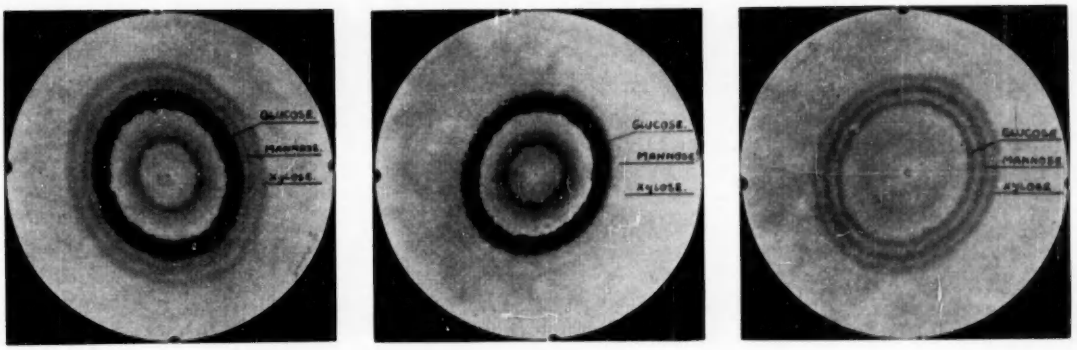
The applicability of the method is demonstrated by the chromatograms shown in Figures 2 and 3. The chromatograms of Figure 2 are of hydrolyzed

* The "radius" of a ring = the mean value between the inner and outer radii.



a b c

FIG. 2. *Chromatograms of hydrolyzed 0.5% HCl extracts of raw vegetable materials.* a—*Fir wood.* b—*Beech wood.* c—*Rye straw.*



a b c

FIG. 3. *Chromatograms of hydrolyzed total rayon pulp, extract, and residue. Pulp,* Uddeholm Alba (*spruce sulfite*); *extraction with 18% NaOH.* a—*Total pulp.* b—*Extracted pulp.* c—*Extract.*

extracts from fir wood, beech wood, and rye straw. The extractions were performed with 0.5% HCl at 100°C for 2 hrs.

The principal component of the hydrolyzate of fir wood is mannose, and that of the other two hydrolyzates is xylose, in agreement with previous statements in the literature. Glucose is a component of less quantitative importance in these hydrolyzates. Further, it appeared from the color of the ring between the xylose and glucose rings that the corresponding sugar in the beech-wood extract is mannose, and in the straw extract arabinose. Characteristic of all three chromatograms is the presence of a galactose ring, probably originating from uronic hemicellulose.

Figure 3 shows what happens on extraction of a rayon pulp with 18% NaOH; it therefore gives an idea of the composition of "technical hemicellulose" and alkali cellulose under idealized conditions. In actual practice, the separation of alkali cellulose and hemicellulose will be less complete than in this experiment, where a twofold extraction with 18% NaOH was applied. The principal components of the hemicellulose are glucose, mannose, and xylose. The inner rings (inside the glucose ring) in Figure 3 (*a* and *b*) originate from disaccharides and perhaps from higher sugars still present in the hydrolyzates.

Investigation of Press and Steeping Lyes

Pulps of various origin.—In the manufacturing process of viscose rayon the steeping liquor is drained after a certain time of steeping. Next the highly swollen sheets of alkali cellulose are pressed. In this operation the "press lye" is removed from the sheets. The composition of this press lye differs from that of the first drained lye in that it has a lower NaOH and a higher hemicellulose content

than the latter; actually, by far the greater part of the hemicellulose to be removed is contained in the press lye. The intensity of pressing is indicated by the pressing factor, which is defined as the ratio of the weight of the pressed alkali cellulose to that of the original bone-dry pulp.

We examined the composition of press-lye hydrolyzates of a rather wide variety of rayon pulps, after steeping in pure 18% NaOH. The press lye was collected between pressing factor values 6 and 3. The total amount of hemicellulose present in 100 g. of press lye was determined in the conventional way by oxidimetric titration; the amounts of the various monomer sugars per 100 g. of press lye were estimated by semiquantitative evaluation of the hydrolyzate chromatograms. The results of this investigation are shown in Figure 4.

It is shown that the total hemicellulose content is always much larger than the sum of the quantities of monosaccharides found in the chromatograms. The explanation of this difference, which is indicated by the blocks "unknown," is probably in the method

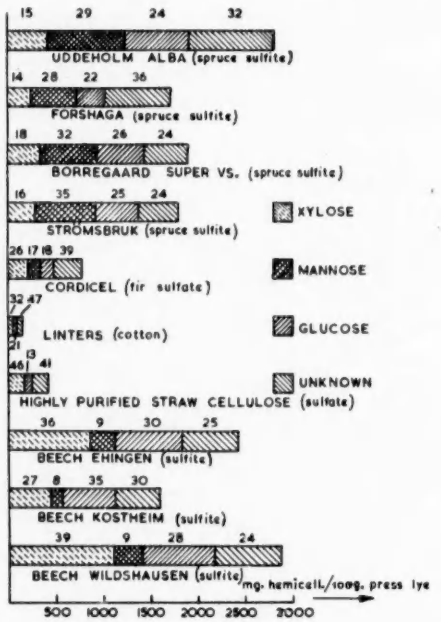


FIG. 4. *Quantity and composition of hemicellulose hydrolyzates in 100 g. of press lye for pulps of various origin. Total length of blocks = quantity (mg.) of sugars present. Figures indicate percentages of individual sugars in the hemicellulose.*

of determination of total hemicellulose. In the conventional hemicellulose determination by oxidation with $K_2Cr_2O_7$ in sulfuric acid, the hemicellulose content is calculated on the basis of the composition $(C_6H_{10}O_5)_x$. It follows from our investigation that part of that which is usually considered as hemicellulose does not consist of short-chain polysaccharides, but of low-molecular-weight, organic substances of other than carbohydrate character. This involves the introduction of certain errors in the numerical values given in this report, which errors may be larger with larger noncarbohydrate content of the hemicellulose. The relative quantities of monosaccharides with respect to each other, as found by the chromatographic method, are, however, not affected. On the other hand, the percentage of "unknown" substance and also the absolute percentages of the monosaccharides in the hemicellulose should be considered uncertain to a certain extent because of the errors introduced in this way.

It is interesting to compare the spruce-pulp press lyes with those of beech pulp. The total hemicellulose contents lie in the same range, but the composition is quite different in the two cases. The relevant percentages are summarized in Table I. The well-known fact that soft woods have a lower xylosan and a higher mannosan content than deciduous woods is clearly reflected in the composition of the hemicellulose found in the press lye of the corresponding pulps.

Although glucose is always present in the hydrolyzates, it never takes a predominant position. Furthermore, it is seen from Figure 4 that, as should be expected, the total hemicellulose content in press lyes from "high-*alpha*" celluloses like Cordicel and the straw pulp investigated is considerably lower than that of normal pulps. The straw-pulp lye is distinguished by the complete absence of mannose. The same is true of the linters press lye, which, moreover, has a very low total hemicellulose content. It is interesting to notice that more than 30% of the linters hemicellulose consists of xylose residues.

TABLE I. PERCENTAGES OF MONOSACCHARIDES IN SPRUCE AND BEECH SULFITE HEMICELLULOSES

	Spruce pulp	Beech pulp
Xylose	14–18	27–39
Mannose	28–35	8–9
Glucose	22–26	28–35
Unknown	24–36	24–30

Influence of pressing factor.—With *Uddeholm Alba* spruce sulfite pulp the concentration and the composition of the hemicellulose in the press lye were determined at various stages of pressing. Figure 5, in which the results are summarized in a cumulative graph, shows the phenomenon, well-known in the manufacture of viscose, that during pressing—*i.e.*, with decreasing pressing factor—the hemicellulose concentration in the lye pressed-out passes through a maximum. Probably in the later stages of pressing, NaOH taken up by the fibers is pressed out.

In Table II are given the percentages of the various sugars, taking the total hemicellulose content of the press lye equal to 100. Obviously, there is no noticeable influence of the pressing factor on the hemicellulose composition.

Influence of NaOH-concentration.—It is known that cellulose shows a different swelling in steeping lye of different concentrations. The swelling increases with increasing lye concentration until it reaches its maximum at about 11%–12% NaOH; thereafter it decreases. The amount of hemicellulose dissolving from the cellulose in the lye corresponds to the degree of swelling.

It was examined whether, with respect to the nature of the polysaccharides, the composition of this dissolved substance varies with the lye concentration. For this purpose, 50 g. of cellulose (*Borregaard Super VS* spruce sulfite) were suspended in 1 liter of lye of the desired concentration; after ¼ hr. stirring the suspension was filtered. The hemicellulose in the filtrate was determined and examined. The results are shown in Figure 6. The glucose curve has a shape similar to that of the total hemicellulose concentration, in contrast with the other monosaccharides. Apparently, the maximum at intermediate NaOH concentrations is caused by dissolution of

TABLE II. PERCENTAGES OF MONOSACCHARIDES IN HYDROLYZATE AT VARIOUS PRESSING FACTORS (PULP, *Uddeholm Alba*)

Pressing factor	Xylose	Mannose	Glucose	Unknown
6.0[5]	18	40	28	14
4.6	17	40	28	15
3.5[5]	14	38	27	21
3.1	18	41	27	14
2.9	20	36	27	17
2.5[5]	17	35	27	21
2.4[5]	21	37	29	13

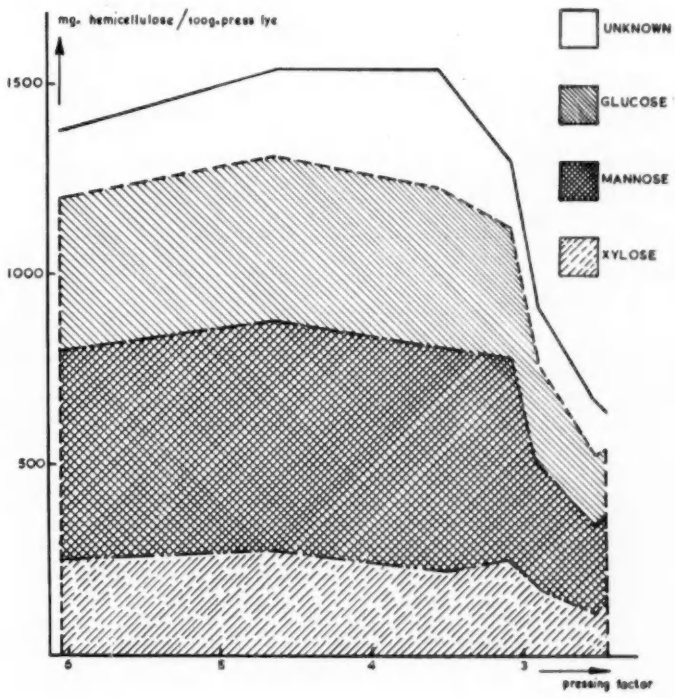


FIG. 5. *Composition of press lye* vs. *pressing factor. Pulp,* Uddeholm Alba.

short cellulose chains. A similar behavior was found with *Uddeholm Alba* pulp.

Influence of steeping temperature.—In a number of experiments with 18% and 21% NaOH as steeping lye, the temperature during the steeping and pressing operations was varied between 15°C and 35°C. No perceptible influence of this variation on the composition of the press lye was found with *Uddeholm Alba* pulp.

Fractionation of press lye.—In a few experiments the hemicellulose in press lye was precipitated in a number of fractions by gradual addition of ethanol. With *Uddeholm Alba* press lye three fractions were obtained in this way, with relative weights 6:9:5. Chromatographic analysis of these fractions resulted in the data presented in Table III.

The residue obtained after the removal of the fractions was evaporated and then hydrolyzed. Since the hydrolyzate contained only a small amount of sugars, mainly xylose, it appeared that the polysaccharide content in the residue was low.

Without more detailed information it is difficult to interpret these results. They might suggest that the hemicellulose present must be considered as a mixture of polymer homologous mannans, xylans, and glucosans, rather than consisting of chains of "copolymer" character. This would be in agreement with the opinion found in the literature, according to which cellulosan is supposed to be a mixture of xylans, mannans, and glucosans.

Dialysis of waste lye.—It is common practice in rayon manufacture to regenerate waste lye from the steeping presses by dialysis. In the dialyzed lye a certain amount of oxidizable material is found in the dichromate titration, corresponding with somewhat less than 0.1% hemicellulose. In order to determine whether or not this reducing substance is of carbohydrate nature, chromatograms were made of waste and regenerated lye from a rayon plant. The waste lye contained 1,000 mg. and the regenerated lye 75 mg. of hemicellulose per 100 g. of lye. The results of the chromatographic analysis are shown in Table IV.

When comparing the values given in Table IV it should be remembered that the NaOH solution becomes appreciably diluted on dialyzing. The con-

TABLE III. COMPOSITION OF HEMICELLULOSE FRACTIONS IN *Uddeholm Alba* PRESS LYE

	Sugars in hydrolyzate		
	Xylose (%)	Mannose (%)	Glucose (%)
Fraction *I*	7	71	22
Fraction *II*	32	40	28
Fraction *III*	48	28	24

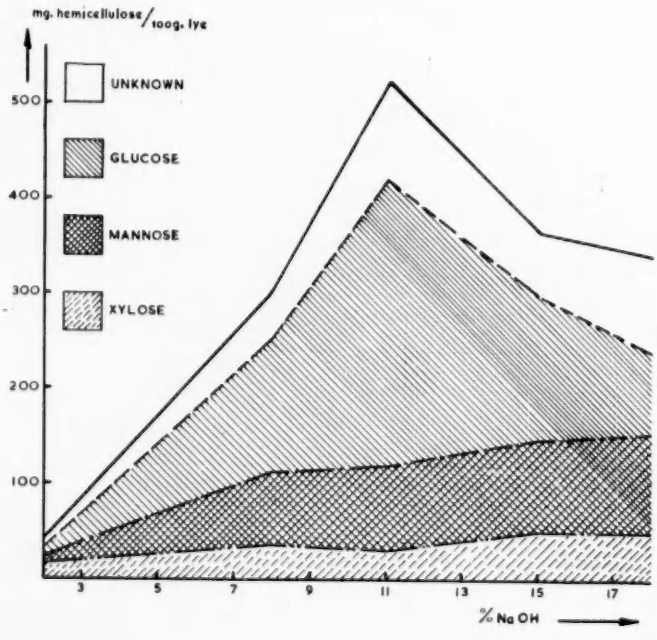


FIG. 6. *Composition of press lye vs. NaOH concentration. Pulp,* Borregaard Super VS.

centration of the waste lye was 17.2% and that of the regenerated lye 7.5%. Therefore, the concentrations given in the second line of Table IV must be multiplied by the factor 2.3 before comparison with those of the first line. It is obvious that even then the sugar concentrations in the regenerated-lye hydrolyzate remain negligibly small as compared to those of the waste-lye hydrolyzate; in other words, the dialysis is quite effective. The remaining reducing substance must be of low-molecular-weight, noncarbohydrate nature; it is certain that organic acids are present in it.

If one assumes that the low-molecular-weight, noncarbohydrate, organic components of the lye pass through the membranes at the same rate as the NaOH, the ratio between the respective concentrations must be the same in the waste lye and in the regenerated lye. The ratio mg. of "unknown" substance per 100 g. to the percentage of NaOH is 11.6 for the waste lye and 10.0 for the regenerated lye, which is in reasonable agreement with this statement.

Figure 7 illustrates the great difference in composition between the organic substance in the dialyzed lye and that in the original waste lye.

TABLE IV. COMPOSITION OF WASTE AND REGENERATED LYE

	Hemicellulose (mg.) per 100 g. of lye	Sugars in the hydrolyzate of 100 g. of lye		
		Xylose (mg.)	Mannose (mg.)	Glucose (mg.)
Waste lye	1,000	215	295	290
Regenerated lye	75	<1.5	<1.5	<1.5

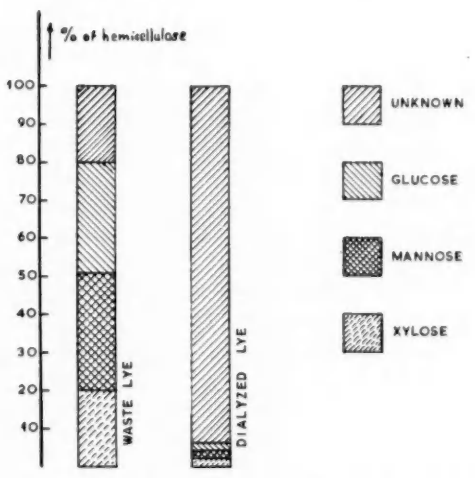


FIG. 7. *Composition of hemicellulose in technical waste lye and regenerated lye.*

Hemicellulose in Unaged and Aged Alkali Cellulose and in Bleached Rayon

White crumbs from *Uddeholm Alba* pulp, before and after aging, and bleached rayon manufactured from them were subjected to alkaline extraction. This was done by preparing slurries of these substances in 17.5% NaOH, the slurries containing 5% cellulose. After ¼ hr. stirring at 20°C, the insoluble material was sucked off, and 200-g. portions of the filtrate were subjected to the usual chromatographic analysis.

From the results presented in Figure 8 it is obvious that the increase in hemicellulose content from aged crumbs to rayon is much larger than that during aging.* In both steps the total increase is due principally to an increasing glucose content of the hydrolyzate and, to a lesser extent, to an increase in "unknown" substance.

The explanation for the difference in quantity and composition of the extractable material between the aged crumbs and the bleached rayon may be of the following: (*a*) further decomposition of cellulose chains during xanthation; (*b*) decomposition of the acid yarn after spinning; (*c*) better diffusion of

* The quantities plotted in Figure 8 correspond to those present in 10 g. of total cellulose.

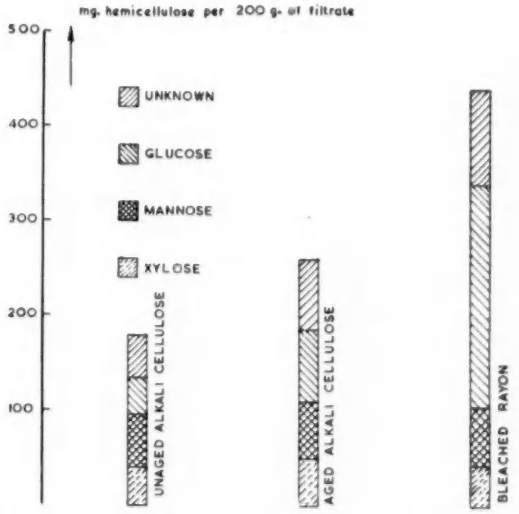


FIG. 8. *Hemicellulose in unaged and aged alkali cellulose and in bleached rayon. Pulp,* Uddeholm Alba.

short cellulose chains from swollen rayon into the lye than from swollen crumbs because of the higher degree of swelling of the regenerated cellulose.* The latter effect would seem to be the most probable explanation. Experiments have shown that decomposition of the acid spun yarn does not take place to a perceptible extent, thus ruling out factor (*b*).

Similar results were obtained with other textile rayons and the corresponding pulps. Tire-cord rayon from a Cordicel-linters mixture behaved somewhat differently in that its hydrolyzate contained less glucose than those of the textile rayons. It remains to be explained whether this is due to the nature of the pulp or to the different spinning conditions when manufacturing tire yarn.

Hemicellulose in the Spinning and Aftertreatment Baths

Although hemicellulose cannot be expected to be soluble in the acid spin-bath, the possibility that small amounts are present in it in a flocculated state should not be precluded. However, chromatographic analysis of a hydrolyzate prepared from a regular textile rayon spin-bath showed that practically no sugars were present.

In the aftertreatment only the alkaline baths are liable to contain hemicellulose. As a matter of fact, it was demonstrated that the sodium sulfide bath used for desulfurizing in a rayon factory contained polysaccharides; in a hydrolyzate from 300 g. of this bath, 10 mg. of xylose, 15 mg. of mannose, and 15 mg. of glucose were found.

General Conclusions

The principal result of this investigation is the proof that commercial rayon pulps contain certain quantities of noncellulosic polysaccharides. The nature and the quantities of these polysaccharides depend on the basic material from which the pulp is prepared and on the pulping process.

A large part of the noncellulosic polysaccharides dissolves during the steeping operation, together with short cellulose chains. The hemicellulose removed with the press lye is therefore a mixture of polysaccharides in which short-chain cellulose is not the quantitatively predominant component. However, part of the hemicellulose will be present in the rayon produced because of incomplete pressing out of the steeping liquor and because of insufficient solubility. This hemicellulose may affect the mechanical properties of the rayon, and may have an influence on such properties as milkiness, dye rate, etc.

Besides various types of polysaccharides, a certain amount of noncarbohydrate, low-molecular-weight, organic substances is dissolved from the pulp on steeping. It is probable that the portion of these compounds which is not removed from the alkali cellulose on pressing will be removed, to a large extent, from the spinning rayon filaments in the spin-bath and during the aftertreatment.

Summary

A chromatographic investigation of hemicellulose in rayon pulps is described. The composition of this hemicellulose, which is essentially a mixture of glucosans, mannans, and xylans, plus low-molecular-weight, noncarbohydrate material, is dependent on the nature of the raw cellulosic material from which the pulp is manufactured and on the type of pulping process used. The hemicellulose found in the intermediate stages of the viscose rayon process originates, for the greater part, from the pulp hemicellulose. This is clearly demonstrated by the high percentages of mannose and xylose found in the corresponding hydrolyzates. The hemicellulose in the spun yarn, however, consists mainly of short cellulose chains. It has been investigated how the quantity and the composition of the hemicellulose in the press lye depends on such variables as pressing factor, NaOH concentration, etc. The hemicellulose present is unaged and aged, alkali cellulose and in the rayon produced therefrom has been analyzed. During the spinning and the aftertreatment of rayon, measurable quantities of hemicellulose are only found in the alkaline sodium sulfide aftertreatment bath.

(*Manuscript received May 12, 1953.*)

* An indication was also found by Wilson, Ringström, and Hedlund (The Alkali Solubility of Pulp, *Svensk Papperstidn.* **55**, p. 37 (Jan. 1952)) that by treatment with diluted NaOH solutions, more cellulose with low D.P. dissolves from regenerated cellulose than from native cellulose.

Some Moisture Relations of Wool and Several Synthetic Fibers and Blends*

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Introduction

The manner in which the wetting and drying behavior of a textile fabric depends upon the properties of the fibers comprising it is of both practical and theoretical significance. The consumer is justifiably interested in the relationship of fiber content to such serviceability criteria as wicking, soilability, wettability, and speed of drying. At the same time, the extent to which the drying of textiles conforms with or departs from theory is of scientific interest, particularly if noteworthy distinctions in behavior among fabrics can be related to intrinsic fiber properties or geometry of the textile structure.

This work was undertaken to answer some practical "consumer-type" questions about fiber-fabric-water relationships. Especially of interest was the extent to which rate of fabric drying might depend upon (*a*) fiber moisture regain, and (*b*) speed of capillary migration.

These and other aspects of the general problem were examined in the light of pertinent theory. A consistent picture of events in wetting-out, extracting, and then drying a fabric may be developed in the context of recent work by Preston and coworkers, Harris and coworkers, Baxter and Cassie, and others.

An attempt to apply certain concepts of classical three-stage drying theory, particularly as adapted by Paul and Wilhelm for textiles, however, was unsuccessful. Observed drying behavior suggests modes of water transport within a fabric during drying somewhat different from those postulated by classical theory. New significance is attached to certain drying-rate curve transition regions in accordance with mechanisms differing somewhat from others previously noted. These mechanisms, as well as the applicability of other current theory, are discussed in connection with the appropriate practical findings described more fully below.

* This research was conducted under the sponsorship of The Wool Bureau, Inc.

The Practical Problem

Suppose two garments of equivalent structure, one containing fibers with a high natural moisture regain and the other of nonhygroscopic fibers, are washed and then hung up to dry. Which one will be dry enough to wear first? Assume, for the moment, that one appears to be dry sooner than the other, and then consider whether the earlier dryness is attributable to: (*a*) originally lower water content at the start of drying; (*b*) more rapid evaporation of water during drying; (*c*) a greater allowable water retention at the time of apparent (palpable) dryness.

At least one of these conditions must be fulfilled for one garment to achieve dryness earlier than the other under similar external drying conditions. Once the foregoing three *symptoms* of drying behavior have been quantitatively assayed, the following fundamental questions pertaining to intrinsic cause arise: (*d*) Are the symptomatic factors favoring earlier dryness (*i.e.*, initial moisture, drying rate, palpable dryness level) uniquely dependent upon the fiber content of the garment? Simply, then, is the rapid-drying fabric claim based on a truly intrinsic fiber property? (*e*) Are the symptomatic factors dependent upon fabric characteristics entirely independent of fiber content? (*f*) Are the symptomatic moisture factors functional with fabric properties which may be critically dependent ultimately upon fiber properties? In other words, is the rapid-drying characteristic of a fabric related to fiber content indirectly because of the influence which such fiber properties as length, diameter, shape, surface, elastic behavior, etc., may have upon the eventual fabric and yarn geometry?

In answer to these questions, it was found for a group of machine-knit fabrics including Dacron, Orlon, Dynel, cotton, wool, and nylon, and wool-nylon and Vicara-nylon blends:

(*a*) Fabrics composed of smooth-surfaced, uncrimped or regularly crimped, and finer fibers have

a higher initial moisture imbibition at total saturation. Three methods of mechanical extraction reduced water content but failed to reverse the trend which indicated that high capallarity of a fabric promotes not only the speed of liquid migration but also greater water retention relative to either fabric void volume or swollen fiber volume. The actual amounts of water retained by a fabric after wetting-out, therefore, appear to be functional with actual total void volume, hydrostatic capillary effects, and methods of mechanical extraction.

(*b*) Irrespective of fiber content and independent of gross geometry, within the limits studied, the fabrics exhibited essentially equal drying rates during the major part of evaporative drying. The absence of "hairiness," as, for example, in a filament fabric, favors a slight increase in evaporation during the constant-rate period. High capillarity seems not to affect net evaporation rates in semistatic convective drying. Intrafiber diffusion, however, is believed to play a part in evaporation phenomena during the dissipation of the last amounts of liquid water, high diffusion tending to arrest the fall-off in rate as the last traces of capillary water are being evaporated.

(*c*) None of the fabrics felt dry until they had been reduced in moisture content to below their respective 100% R.H. equilibrium regain values. In most instances the psychophysical sensation called "dampness" (which may also include coolness and so on) disappeared for the several fabrics at a regain value well above equilibrium with 65% R.H.

In regards to questions (*d*), (*e*), and (*f*), it is concluded that length of time to dry depends principally upon the amount of initial liquid water retained by a fabric per unit area for evaporation. The amount of water is related to the void volume of the fabric, a gross geometric factor, and capillarity, a fiber-related fabric characteristic. The fiber-sorbed water is relatively inconsequential to the practical problem of length of time to dry.

The significant influence of fiber properties is believed to be the manner in which fiber shape and surface reflect in increased or depressed capillarity of the fabric eventuating as enhanced or diminished water uptake on wetting and retention on mechanical extraction. Fabric surface hairiness, which has a minor influence on evaporation rate, may be dependent upon both fiber and fabric geometry properties. High moisture permeability may promote more rapid drying-out of final traces of liquid water.

Experimental Procedure and Data

Material Investigated

Seventeen different samples of machine-knit men's socks were studied for their moisture takeup and drying characteristics. These are described in Table I. Several different samples of men's tropical suiting fabrics differing in fiber content but as nearly

TABLE I. QUALITATIVE DESCRIPTION OF SOCKS

Code	Fiber	Length	Rib Width	Rib Height	Condition
X-12	wool	ankle	none		worn
X-13	wool*	ankle	medium	high	new
X-14	wool*	ankle	medium	flat	new
X-15	wool*	low ankle	narrow	moderate	worn
X-16	wool*	high	narrow	high	new
Y-11	wool*	ankle	medium	medium	worn
X	nylon staple	ankle	heavy cable		worn
Q	nylon staple	semihigh	wide	medium	new, solvent-extracted
C-5	nylon staple	ankle	medium	medium	worn
Y	nylon staple	ankle	medium	flat	worn
Z	nylon filament	low ankle	none		worn
D-1	Orlon staple	ankle	wide	flat	worn
E-6	Dacron staple	high	medium	high	worn
C-2	Dynel	ankle	narrow	flat	worn
G-4	Vicara/nylon	ankle	medium	medium	worn
B-10	wool/nylon	ankle	wide	high	worn
—	cotton	high	medium	flat	worn

* Shrink-resistant or shrinkproofed by various methods.

alike in structure as obtainable and several of the sock samples were examined for capillary migration and wicking effects.

Major Physical Attributes (Table II)

Specimen weight.—The weight of each sock was determined at equilibrium with 65% R.H. and 70°F after 48 hrs. conditioning. The moisture sorbed at these conditions is considered, for all practical purposes, as part of the intrinsic fiber mass. Thus, a wool fabric at equilibrium with 65% R.H. may consist, by weight, of 85% keratin (etc.), 2% dye, and 13% water; a Dacron fabric may consist of 96% polyethylene terephthalate, 3% dye, and 1% H_2O. For our purposes, these are, respectively, a "dry" wool fabric and a "dry" Dacron fabric. However, bone-dry weights were also determined and used for determination of moisture regain values.

Specimen area.—The projected area of each sock specimen was determined by laying it flat and tracing its silhouette. Since the sock in this form is actually a double thickness of fabric, the area found is actually about half the total area of the external surface of the specimen. The specimens were laid out to present the same configuration as when hung loosely for evaporation, without any intentional stretching or rationalization for the topographical effect of ribs and valleys.

Specimen thickness.—Thickness was measured on the double layer of fabric, with the socks laid flat in the same manner as for the area measurement. An Ames Randall Stickney dial instrument with a 1.25-in. diameter presser foot was used. Over-all thicknesses were measured at the sole (nonribbed) in a pressure range corresponding primarily to "wild" fiber compression with a minimum of bulk compression.

Fabric volume.—The dry fabric volume was found simply by multiplying projected area by thickness. Some error in this value must be expected because the projected area does not entirely account for the fraction of surface involved in the rise and fall of the ribbing. However, the error is not considered to affect the results significantly, since all but two specimens (*X-12* and *Z*) had ribbing.

Quantitative Measures of Moisture Behavior

Initial moisture content.—

Wetting-Out: Each specimen was soaked in a mild soap solution for ½ hr. After soaking, the soap solution was decanted and the socks were rinsed first in warm and then in cold water. When no air

TABLE II. MAJOR PHYSICAL PROPERTIES OF SOCKS

Code	Fiber	Conditioned weight* (g.)	Dry projected area (sq. cm.)	Thickness† (cm.) Wet	½ Dry	Dry	Fabric volume (dry) (cc.)	Fiber volume (cc.)‡ Dry	Wet
X-12	wool	25.2	355	.277	.277	.328	116	19.1	25.6
X-13	wool	25.4	316	.251	.272	.290	92	19.2	25.7
X-14	wool	26.4	323	.292	.305	.348	113	20.0	26.8
X-15	wool	41.0	374	.526	.518	.592	221	31.1	41.6
X-16	wool	35.3	419	.250	.250	.287	120	26.7	35.8
Y-11	wool	28.6	330	.236	.254	.272	90	21.7	29.1
X	nylon	27.1	316	.356	.384	.424	134	23.8	26.2
Q	nylon	22.4	361	.201	.198	.213	77	19.6	21.6
C-5	nylon	17.8	323	.152	.165	.188	61	15.6	17.2
Y	nylon	21.2	368	.190	.190	.208	77	18.5	20.4
Z	nylon	9.7	200	.155	—	.150	29	8.5	9.4
D-1	Orlon	21.0	297	.203	.206	.221	66	17.9	17.9
E-6	Dacron	28.6	426	.203	.208	.226	97	20.7	20.7
C-2	Dynel	20.4	355	.147	.157	.168	59	15.6	15.6
G-4	Vicara/nylon	20.2	330	.157	.165	.188	62	16.8	20.2
B-10	wool/nylon	28.9	342	.254	.257	.302	103	23.5	28.2
—	cotton	20.5	419	.124	.122	.142	59	13.2	17.2

* Equilibrium with 65% R.H.
† Nonribbed region at 18 g./cm.² pressure; includes two layers, as in projected area measurement.
‡ Calculated.

bubbles were produced upon squeezing under water, the socks were considered wet-out.

Removal of "Excess" Water: Three methods of removing the excess water retained by the wet-out specimens were tried. The relative behavior of each sock under the different extraction methods is considered a drying characteristic of some consequence in itself. The three alternative methods were squeezing, centrifugation, and simple drainage.

(*a*) Squeezing: After wetting-out, the socks were run through a rubber-roll laboratory pad. Pressure was maintained by spring tension. Socks were weighed immediately after squeezing.

(*b*) Centrifugation: Wet-out socks were "spun-dried" in a Bendix home-laundry machine for 5–6 min. and then weighed.

(*c*) Simple drainage: Wet-out socks were suspended vertically for 15 sec. and then laid flat on a double thickness of dry paper towelling for 2 min. on each side. Weighing was made immediately following the 15-sec. vertical suspension and then after drainage on the towelling.

The amounts of water retained in the wet-out and extracted socks as determined by the three methods are given in Table III.

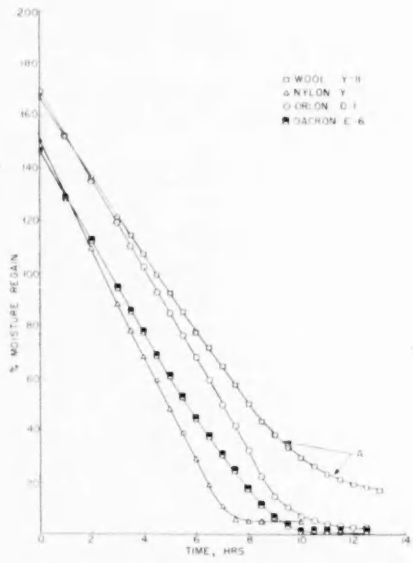


FIG. 1. *Course of drying from saturation; typical time vs. regain curves.*

The initial moisture content as a symptomatic drying-rate property is later discussed and related to fiber content and fabric characteristics.

Drying rate.—The socks, wet-out and drained on paper towels as described above, were hung on a wooden indoor drying rack in the conditioned laboratory (65% ± 2% R.H., 70° ± 2°F). Weighings were made at ½-hr. and 1-hr. intervals as drying progressed. The moisture regain as a percentage of the bone-dry sock weight was calculated and then plotted against time. Several typical drying curves are given in Figure 1. Drying rates, expressed as % weight loss per hour during the initial constant period are given in Table IV. These values are subsequently to be rationalized on the basis of weight loss/unit area/hour.

Point of palpable dryness.—During the latter part of the drying process the feelings of "wetness" and "dryness" of each sock were noted. The points at which the socks no longer felt "damp" are marked on Figures 7–10 by arrows and tabulated in Table IV.

Rate of Capillary Migration

Two techniques were employed in measuring the speed of capillary migration in fabrics of differing fiber content. In one method, 6 in. × 1 in. warpwise

TABLE III. TOTAL UPTAKE AND RETENTION OF WATER BY SOCKS

Code	Fiber	Sorbed in fiber* (g.)	Total water retained† (g.) Satu-rated	Drained	Towel-Squeezed	Bendix
X-12	wool	4.1	65	48	20	24
X-13	wool	4.2	54	40	17	18
X-14	wool	4.3	75	55	17	21
X-15	wool	6.7	128	88	32	31
X-16	wool	5.8	75	54	26	28
Y-11	wool	4.7	62	38	—	—
X	nylon	1.5	97	75	24	25
Q	nylon	1.2	55	30	15	13
C-5	nylon	1.0	42	26	11	18
Y	nylon	1.2	55	30	18	16
Z	nylon	.6	18	12	—	—
D-1	Orlon	1.1	60	34	23	24
E-6	Dacron	.09	83	41	21	21
C-2	Dynel	.01	51	33	14	23
G-4	Vicara/nylon	3.4	42	30	13	17
B-10	wool/nylon	3.0	73	53	18	22
—	cotton	3.1	58	47	—	—

* Calculated from difference in regain moisture 65% R.H. to 100% R.H.

† Gross weight increase over conditioned weight.

strips of tropical suiting fabric were hung above a beaker of distilled water with their lower ends held submerged by means of a brass weight. Strips of pH paper clipped to the dry fabric at regular length intervals indicated the arrival of liquid water as capillary rise progressed. The fabrics employed in this experiment are described in Table V, and the relative rates of capillary rise are illustrated in Figure 2 for fabrics both as received and after scouring with A.A.T.C.C. scouring liquor.*

A second method for approximating the ease of penetration entailed measuring the time for complete dissipation of a small drop of water. The water was deposited by means of a buret from a height of 1 cm. onto a strip of fabric held out horizontally. The fabrics in one series were laid on absorbent towelling, and in a second experiment they were suspended between two supports without any backing surface beneath the region upon which water was deposited. The time was measured from the first instant of contact of water until the droplet had run away horizontally into the fabric, leaving only a wet spot. Data for this method on the several suiting and sock fabrics tested are given in Table VI.

* "Technical Manual," Tentative Test Method 25–52: 30-min. boil in carbon tetrachloride containing, per liter: 5 cc. dry-cleaning soap, 4 cc. butyl alcohol, and 4 cc. distilled water.

Bases for Calculation

The amount of water retained in a fabric is traditionally expressed as some function of the fabric

TABLE IV. DRYING AFTER TOWEL-DRAINAGE

		Initial moisture*			Drying rate (constant period)	Moisture content at end of constant period			Moisture at palpable dryness
Code	Fiber	Regain (%)	Liquid water† (cc.)	Void occupied (%)	(% fiber wt./hr.)	Regain (%)	Liquid water† (cc.)	Void occupied (%)	(% regain)
X-12	wool	236	44	45	19.7	55	4.4	4.5	30
X-13	wool	195	36	49	15.4	58	5.1	7.0	27
X-14	wool	255	51	55	15.4	—	—	—	—
X-15	wool	260	81	43	15.3	—	—	—	—
X-16	wool	192	47	52	14.7	55	6.1	6.6	23
Y-11	wool	167	33	49	14.6	49	3.5	5.1	26
X	nylon	293	74	67	16.6	—	—	—	—
Q	nylon	144	29	51	19.2	27	3.4	6.0	5.6
C-5	nylon	160	25	56	22.2	27	2.7	6.0	5.4
Y	nylon	151	29	50	20.4	22	2.2	3.8	5.1
Z	nylon	132	11	54	27.1	40	3.0	14	5.1
D-1	Orlon	169	33	69	16.8	19	3.7	7.7	3.1
E-6	Dacron	146	41	54	16.4	25	7.1	9.3	0.7
C-2	Dynel	160	33	76	19.7	25	5.1	11.9	0.1
G-4	Vicara/nylon	177	27	59	21.6	24	1.0	2.2	12
B-10	wool/nylon	213	50	63	16.0	30	3.2	4.1	16
—	cotton	259	44	95	26.1	40	1.8	3.9	14

* Towel-drained.
† Total water less fiber-absorbed water.

TABLE V. TROPICAL SUITING FABRIC PROPERTIES

			Texture		Weight (oz./60 in. width/yd.)	Yarn plies	
Code	Fiber	Weave	Warp	Filling		Warp	Filling
1	100% wool	plain	53	46	9.4	2	2
4	85% wool-15% nylon	plain	47	47	10.0	2	1
5	80% wool-20% nylon	plain	54	42	9.6	1	1
7	45% wool-55% Dacron	plain	57	46	8.8	2	2
8	100% Dacron	plain	62	46	9.3	2	2

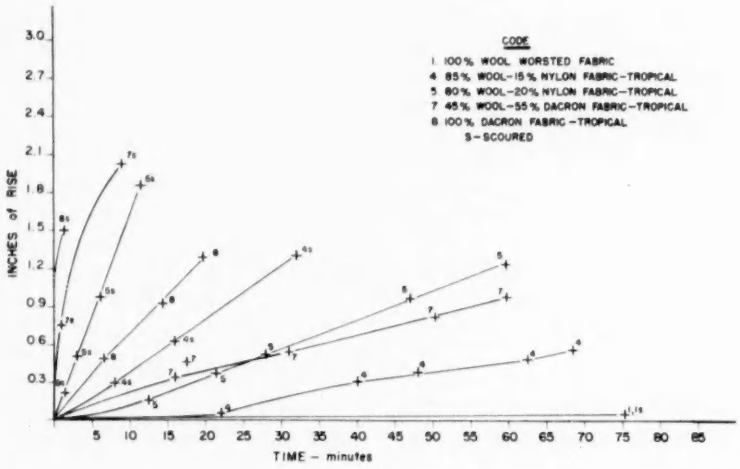


FIG. 2. *Rate of capillary rise at room temperature in several similar suiting fabrics differing in fiber content, before and after scouring.*

TABLE VI. TIME FOR DISSIPATION OF WATER DROP

Code	Fabric	Time for dissipation: Absorbent-backed	Time for dissipation: Air-bridge
1	wool tropical (as received)	2 hrs. +	2 hrs. +
1	wool tropical (scoured)	1.5 hrs.	2 hrs. +
4	85% wool-15% nylon (as received)	57 min.	2 hrs. +
4	85% wool-15% nylon (scoured)	16 min.	2 hrs. +
5	80% wool-20% nylon (as received)	33 min.	1 hr.
5	80% wool-20% nylon (scoured)	4.5 min.	10 min.
7	45% wool-55% Dacron (as received)	35 min.	38 min.
7	45% wool-55% Dacron (scoured)	16 sec.	50 sec.
8	100% Dacron (as received)	3.8 min.	30 min.
8	100% Dacron (scoured)	12 sec.	40 sec.
X-15	wool sock, worn		2 hrs. +
E-6	Dacron sock, worn		10 sec.
D-1	Orlon sock, worn		10 sec.

weight. This is a valid, useful, and convenient method for many purposes. Data of this sort are given in several of the accompanying tables and graphs. Unfortunately, neither weight % moisture content nor % regain of a wet-out fabric is a very revealing criterion to apply in studying the relative effects of fiber and fabric properties on degree of fabric saturation.

It is quite obvious that any water beyond that actually sorbed in the fibers must be retained as liquid water within the voids of the fabric structure. Generally, such free volumes are considerably greater than the volume of fibers which provide the space matrix of the fabrics. For the liquid water held in a fabric, the fiber network constitutes an elaborately shaped vessel with (perhaps) peculiar and specific wall properties.

One would certainly not express the contents of a beaker as a percentage of the weight of the glass (or stainless steel, or polyethylene, etc.). A 200-cc. beaker is half-filled when it contains 100 cc. of water. Similarly, a study of the water content of a water-fiber system, when large fractions of total moisture are present as liquid, should logically take into account the available void volume of the fabric.

In the present work, therefore, an attempt has been made to describe moisture content in the several conditions of wetting in te ms of the percentage occupation of available volume. The size, shape, distribution, and availability of the spaces may be controlled by both fiber characteristics and fabric construction. The relative significance of each of these in determining the amount of water held by a fabric is the present object of investigation.

Just as the available space for liquid occupation is of concern in the study of water content, so is the available surface of consequence in the analysis of evaporation rates. One would not discriminate between the evaporation rates of water from two vessels on the basis of weight loss as a percentage of the vessel weights. One-hundred cc. of water will evaporate in one-third the time from a petri dish of 300 sq. cm. area as it would from a beaker of 100 sq. cm. area. Yet, in both cases, evaporation proceeds at the same rate in units of weight/area/time.

TABLE VII. CONTACT ANGLES FOR SEVERAL FIBERS [25]

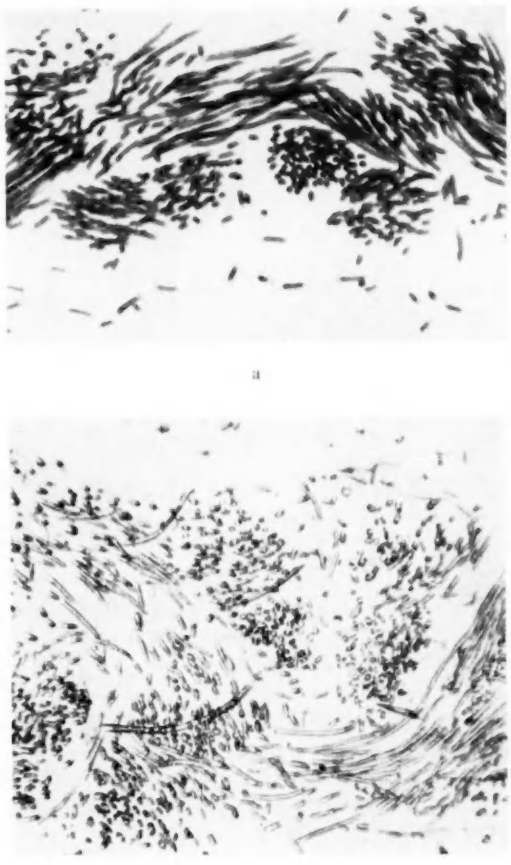
nylon, Vinyon, Vinyon N, Terylene, Orlon, casein, wool	45°–50°
cellulose acetate	15°–35°
Ardil (wool scoured)	10°
viscose	0°
viscose (steamed at atmospheric pressure)	45°–50°
viscose (steamed at 30–35 lbs. pressure)	55°–60°
viscose (Velanized)	110°
viscose blank as for Velanizing	60°

Therefore, if evaporation rate phenomena are to be ascribed either to fabric or to fiber properties, they must be considered in terms of rational units that account for exposed external areas of fabric. This method was employed under similar circumstances of drying by Fourt *et al.* [9], and many of their results are confirmed. Ultimately, the speed of drying is to be directly related to the volume of water retained in a fabric and the area available for evaporation of this water.

Wetting Phenomena: Uptake, Wicking, Extraction

It is a common misapprehension that nonhygroscopic fibers (*i.e.*, those of low intrinsic affinity for moisture vapor) will automatically produce a hydrophobic fabric. Baxter and Cassie [2], in developing a theory of fabric water-repellency, pointed out the major significance of the fine geometry of a textile structure in contributing to resistance to water penetration. They stated: "The requirements of a water repellent fabric are (*a*) that the fibers shall be spaced uniformly and as far apart as possible and (*b*) that they should be held so as to prevent their ends drawing together. . . . Wetting takes place more readily on surfaces of high fiber density and in a fabric where there are regions of high fiber density such as in yarns, the peripheries of the yarns will be the first areas to wet out and when the peripheries are wetted, water can pass unhindered through the fabric." They demonstrated that the ease of penetration, which controls both the extent of liquid uptake and the speed of capillary migration, is primarily dependent upon the spatial disposition of the fiber surfaces.

High contact angles of wetting of fiber surfaces will impede wetting if the fabric geometry takes advantage of this effect. Again, however, there is no categorical necessity that a nonhygroscopic fiber be hydrophobic. Indeed, wool, one of the most hygroscopic fibers, has been described as hydrophobic



a

b

FIG. 3. a—*Cross section through knitted nylon fabric.* b—*Cross section through knitted wool fabric.*

[26]. Table VII, from Preston and coworkers, gives the receding angle of contact for most of the fibers employed in this work. It will be seen that, at least insofar as the receding angle is concerned (which controls moisture retentivity), the hygroscopic and nonhygroscopic fibers hardly differ.

A significant finding in the present work is that wool fabrics consistently are less thoroughly saturated with water than the others after equivalent wetting and extracting conditions (Table VIII). The uniformly low bulk density throughout a knitted wool fabric is illustrated by the cross-sectional photomicrograph of Figure 3b, as contrasted with one of the staple nylon fabrics (Figure 3a). It is likely that the three-dimensional crimp and irregular fiber

TABLE VIII. LIQUID WATER CONTENT AS % OF FIBER AND VOID VOLUMES

Code	Fiber	Volume (cc.) Void*	Volume (cc.) Fiber†	H_2O as % of void volume Saturated	Drained	Squeezed	Bendix	H_2O as % of fiber volume Saturated	Drained	Squeezed	Bendix
X-12	wool	97	25.6	63	45	16	21	240	170	62	78
X-13	wool	73	25.7	70	49	18	19	190	140	50	54
X-14	wool	93	26.8	76	55	14	18	260	190	47	62
X-15	wool	190	41.6	64	43	13	13	290	200	61	58
X-16	wool	93	35.8	77	52	22	24	190	130	56	62
Y-11	wool	68	29.1	84	49	—	—	200	110	—	—
X	nylon	110	26.2	87	67	20	21	360	280	86	90
Q	nylon	57	21.6	94	51	24	21	250	130	64	55
C-5	nylon	45	17.2	91	56	22	38	240	150	58	100
Y	nylon	58	20.4	93	50	29	26	260	140	82	73
Z	nylon	21	9.4	83	54	—	—	190	120	—	—
D-1	Orlon	48	17.9	123	69	46	48	330	180	120	130
E-6	Dacron	76	20.7	109	54	28	28	400	200	100	100
G-2	Dynel	43	15.6	118	76	32	53	330	210	90	150
G-4	Vicara/nylon	45	20.2	86	59	22	30	190	130	50	67
B-10	wool/nylon	79	28.2	89	63	19	24	250	180	53	67
—	cotton	46	17.2	119	95	—	—	320	260	—	—

* Void volume of conditioned sock.
† Water-swollen, calculated.

surface of wool maintains sufficient openness of yarn structure to provide the conditions recommended by Baxter and Cassie for water-repellency.

Intuitively, one might expect an open yarn to be more penetrable; but consider that capillary migration depends for its function upon continuous, long, narrow pores. Yarns spun from smooth-surfaced, more regular fibers are inclined to present localized dense regions for easier initial wetting by aqueous films. Secondly, the same fiber characteristics will regulate fabric fine geometry in the direction of long and continuous, albeit twisted, capillary pores necessary for thorough and rapid penetration.

The speed of capillary migration, or wicking, is a behavior characteristic of apparel fabrics of some note in itself. Stains and liquid-dispersed soils are probably more thoroughly and rapidly carried into finer recesses and over wider areas in fabrics of high capillarity. Similarly, simple water-wetting, such as in a rain shower, will be more thorough and will carry *through* a fabric as well as *along* it, at perhaps an uncomfortable rate to the wearer. Increasing the fiber-to-water contact angle by suitable surface treatments may be effective in reducing the effects of close and regular fiber packing, however.

The speed of capillary rise in several equivalent suiting fabrics of different fiber content is illustrated by Figure 2. Each fabric was tested both as received and after a scour to remove surface finishes. The effectiveness of the latter is apparent. However, the extremely low capillarity of the all-wool fabric is striking, both in the vertical rise method (Figure 2) and in the time for complete absorption of a drop of water (given in Table VI). Increasing amounts of nonwool fiber in blends appears to have an additive effect in the direction of higher capillarity.

The amounts of liquid water retained after three different methods of mechanical extraction are given in Table VIII for the sock fabrics. The methods are considered somewhat comparable to the housewifely techniques of rolling socks in a towel, wringing either by hand or by machine, and centrifuging in a standard model home-laundry machine. There is no doubt that more or less water will be left behind in the fabric voids depending upon the effort exerted to remove it. Certainly higher centrifugal fields than those obtained in the Bendix machine will reduce the water content more effectively.

Preston [24, 25, 26], however, has shown that even under 1,000 *G*'s for 5 min. considerable volumes of liquid water may be retained in the finer capillaries of a textile structure. The reduction in amount of residual water with increasing force of extraction may well differ from one assembly of fibers to another depending upon the diameters of the fibers, fiber shape, fiber-water contact angle, sur-

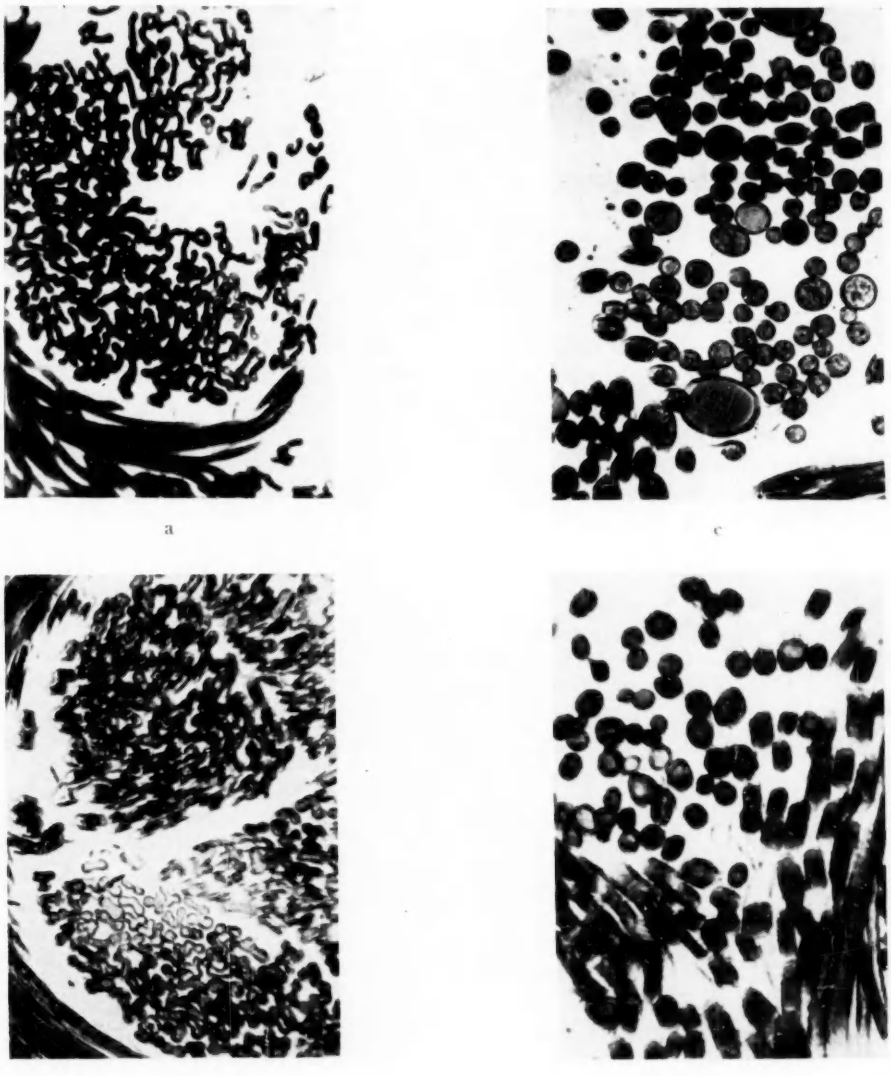


FIG. 4. *Cross-sectional photomicrographs through yarns in socks (magnification, 150 ×).* a—*Dynel.* b—*Orlon.* c—*Nylon C-5.* d—*Wool Y-11.*

face tension of the water, and the orientation of the fibrous mass.

In any event, insofar as the practical considerations of the present problem are concerned, three reasonably realistic methods of extracting liquid water from quite realistic end-use textile items were tried. It is indicated that the course of evaporative drying would be initiated with substantial volumes of liquid water retained in the fabrics.

These volumes of water are rather consistently related to the available void volumes of the fabric. Simple drainage leaves between $\frac{1}{2}$ to $\frac{3}{4}$ of the fabric voids filled with water. Squeezing or centrifuging reduces this to about $\frac{1}{3}$ to $\frac{1}{4}$ void occupation in most instances. Among the exceptions to this are the particular Orlon and Dynel fabrics employed. The consistently higher % volume retention of liquid water of these fabrics may be explained, in part, in

terms of the photomicrographs of Figure 4. It is likely that the smaller fiber diameters and interlocking cross sections of the Orlon and Dynel fabrics provide finer capillaries, which are more difficult to empty, in at least qualitative concordance with the predictions of Preston [26]. Probably the regularity and continuity of capillaries, which cannot be determined by cross-section analysis, also contribute to the occasional high water-retentivity of some of the other fabrics.

The Course of Evaporative Drying

Classical Three-Stage Theory

Most theories for the evaporation of liquid water from a saturated, porous substrate provide three periods. It is generally found that evaporation during the course of drying from saturation in a constant atmosphere proceeds first at an essentially constant rate. After the total moisture content has been reduced below a particular threshold, the rate begins to decrease—first linearly and eventually in some nonlinear manner with the residual moisture content. A number of possible mechanisms which may control the over-all process have been described [3, 4, 6, 10, 20, 22, 27]. The essential features of most of these follow:

Constant-rate period.—During this period the substrate presumably starts out entirely saturated with moisture, and evaporation occurs from a continuous water-air interface at the periphery of the substrate. Energy for evaporation and the water mass are exchanged across this interface as evaporation transpires. Conditions are analogous to water evaporating in a beaker, and the phenomena are governed by relatively simple thermodynamic principles. With external conditions such as air flow velocity and temperature constant, the grams of water departing per unit of time will remain constant and proportional to the actual area of liquid interface.

First falling-rate period.—By virtue of the evaporative loss of liquid water, it is inevitable that the previously continuous liquid surface will eventually begin to retreat below the highest protuberances of the porous medium. A so-called "critical moisture content" is eventually achieved, at which time the original steady-state heat and mass transfer conditions no longer prevail. From this point until a second so-called "falling-rate period" sets in, the evaporation rate in grams/hour/square centimeter of substrate periphery falls in direct proportion to the total residual moisture held within the body of the porous substrate.

The critical moisture content is considered, by this argument, to be the minimum concentration of water at which capillary rise to the air-liquid interface remains sufficiently rapid to maintain the original maximum peripheral surface of evaporation. At the critical moisture content the exposed liquid surface decreases in area, and, consequently, the rate at which water departs in grams/hour/square centimeter of exposed area of substrate decreases proportionately as the wetted fraction of the total exposed area decreases.

During this period the intrinsic evaporation rate may remain a constant in items of grams/square centimeter of true interface, but this true interface is gradually diminishing in area. Capillary motion of water from the liquid reservoir in the substrate, which until this time is supposed to have been replenishing the evaporate at the substrate surface, no longer can keep up with the total evaporative loss of water. If the net rate of evaporation is low, the constant-rate period may be prolonged, and, conversely, with low capillary migration and high net evaporation rates, the critical moisture regain occurs earlier.

Second falling-rate period.—The transition from the first to the second falling-rate period is rarely clear-cut. Moreover, the second falling-rate period is not characterized by a linear dependence of rate upon moisture content. Various explanations have been given for the phenomena occurring at the transition from the first to the second falling rate-periods and during the second falling-rate period. In one version [20], the latter period begins at the instant of total depletion of liquid water and the onset of desorption of regain moisture. For nonhygroscopic granulated solids such as sand [3], this period is believed to coincide with the breaking up of capillary films, when further evaporation is from isolated pockets of liquid between grains. In any event, the final stage of drying entails a possible multiplicity of effects, with perhaps two or more conditions contributing to the net evaporation process.

Paul and Wilhelm, in a study of the radiation-drying of textiles, attempted to apply many of the foregoing concepts. The three-stage drying mechanism put forth by these authors is probably insufficient to explain certain effects noted in the present work. The difficulty resides mainly in a delineation of the modes by which moisture migrates

in, is lost from, and is retained within the textile structures during the second and third stages, and particularly the nature of the transition between these stages.

Proposed Departures from Classical Theory

It is believed, first, that the constant rates observed in the present work cannot depend upon the existence of a single liquid-air interface maintained by capillary migration from the core to the surface of a fabric. Rather, the liquid-vapor interfaces throughout the entire wetted lattice of fibers are considered to maintain a constant reservoir of saturated vapor on one side of a boundary film of stagnant air which exists at the external surfaces of the fabrics. Diffusion of water vapor from the continuously near-saturated internal atmosphere of the fabric to the ambient environment proceeds at a constant rate consistent with the energy gradient across the film [9]. This gradient is determined by the temperature differential between the fabric and the external atmosphere. The fabric temperature, in turn, is regulated by the ease with which the internal atmosphere can be maintained saturated (or nearly so) by the internal evaporation from liquid films on fibers into the fabric voids. During the constant-rate period a steady-state balance is achieved between internal evaporation rate, internal vapor pressure, and fabric temperature.

Second, the final falling-rate period is not felt to be initiated at the instant of total depletion of liquid water and the onset of fiber substance desorption. Actually, the fall in over-all rate starts while there are still significant amounts of liquid water present in interfiber capillaries, and while the internal atmosphere is still at a concentration of 99 + % R.H. However, further evaporation of liquid water from trapped capillaries or from concave liquid surfaces into the fabric void atmosphere requires the fabric temperature to rise. In the shifting dynamic equilibrium, the increased difficulty of internal evaporation reduces the thermal gradient across the fabric surface boundary film. The internal vapor phase remains substantially saturated but only at the expense of a lower rate of energy transmission through the boundary film, and hence a reduced over-all evaporation rate.

Third, until the final falling-rate period sets in, internal evaporation occurs essentially from liquid surfaces. When the residual liquid, however, is eventually held mainly in trapped capillaries, or beneath concave liquid surfaces, saturated fiber surfaces may become sites for internal evaporation. Intrafiber diffusion of water from surfaces wetted by trapped or capillary water to nonwetted surfaces exposed to the void atmosphere can be expected. If this diffusion-evaporation can occur rapidly enough, the downward shift in over-all mass-energy transfer rates may be slowed up or even arrested at a new dynamic equilibrium level before all the liquid water is dissipated. Fabric temperature will not rise as rapidly since the internal atmosphere of the fabric can be maintained at near-saturation more easily in spite of reduced evaporation from liquid water surfaces. Such intrafiber diffusion is believed to account for a double inflection in the wool fabric drying rate curves just prior to final fiber desorption.

It was noted previously that certain fiber characteristics promote rapid capillary migration during the wetting of a fabric. It might be supposed, in the light of classical drying theories, that such marked differences in capillarity as were observed would produce some detectable differences in drying behavior during the period when considerable amounts of liquid water are present.

Consider, however, the data of Table IX, which recapitulates drying rates of the socks during the

TABLE IX. NET EVAPORATION RATE DURING CONSTANT PERIOD AND LIQUID-FIBER VOLUME RATIOS

Code	Fiber	Evaporation rate (mg./sq. cm./hr.)	Liquid volume at end of constant period (% of fiber volume)
X-12	wool	6.3	17
X-13	wool	5.6	19
X-14	wool	5.5	—
X-15	wool	5.6	—
X-16	wool	5.4	17
Y-11	wool	5.5	12
X	nylon	5.1	—
Q	nylon	5.7	16
C-5	nylon	5.9	16
Y	nylon	5.7	11
Z	nylon	6.6	32
D-1	Orlon	5.6	20
E-6	Dacron	5.5	34
C-2	Dynel	5.6	33
G-4	Vicara/nylon	6.1	5
B-10	wool/nylon	5.7	11
—	cotton	5.7	10

major portion of the drying process on the rational basis of weight of H_2O lost/unit area/unit time. It is apparent that such wide differences in capillarity as are illustrated by Figure 2 and Table VI are in no way reflected by wide divergencies in initial drying rates. Moreover, these initial rates remained substantially constant for each sock from the point of near-saturation until there was only sufficient water left to occupy about 5%–10% of the void volume (Table IV) or about 10%–20% of the fiber volume (Table IX).

The nylon fil, Dacron, and Dynel socks—all of which might be expected to exhibit rapid capillary migration of liquid water to any hypothetical constant liquid-air interface—manifest the first significant decrease in drying rate when they contain as much liquid water as 30% by volume of fiber. Capillary migration was still possible in all the socks at the termination of their respective constant-drying-rate periods. Preston and Bennett [23] have shown that this migration may occur even down to the point of practically negligible liquid film in the fiber assembly.

It would certainly seem that, as far as practical household drying of the socks is concerned, the high capillary effect of smooth, uniform fibers does not promote high evaporation rate. There were, however, four socks in the group tested which exhibited initial constant rates slightly greater or less than the majority. One all-wool sock (*X–12*), the nylon filament sock (*Z*), and the Vicara-nylon blend (*G–4*) had rates somewhat greater than could be accounted for by experimental error, and one spun-nylon sock (*X*) had a somewhat lower than average rate.

Examination of the fabric surfaces of the socks which had higher rates revealed a sparsity of "wild" fibers (as one would certainly have expected, in any event, for the filament yarn fabric). At the other extreme, the spun-nylon sock, which manifested the lowest drying rate in the entire group, had the "hairiest" surface in the group. These observations bear out one of the conclusions reached by Harris and coworkers [9] that hairy-surfaced fabrics may have somewhat lower drying rates.

Now, with differences in capillarity apparently ineffectual in producing differences in drying rate both from fabric to fabric and in any one fabric from near-saturation down to 5% occupation of voids by liquid water, what can be the mechanisms controlling drying? Particularly, why is rate as constant as it is among the several different fabrics, and to what can the few relatively minor divergencies in constant rate be ascribed?

Mechanisms Early in Drying

Imagine the voids in a fabric such as illustrated by Figure 3 to be about half-filled with liquid water. The liquid water would be distributed throughout the fiber latticework enclosing groups of fibers, as illustrated by the idealized conception of Figure 5(a). The enclosed volume of water in such an assembly is retained within as convex a liquid surface as can be achieved by surface tension. Evaporation from the fiber-water assembly into the surrounding free space in the void volume of the fabric proceeds freely. The atmospheric "well" in the body of the fabric is maintained saturated with water vapor at a constant "wet-bulb" temperature until the

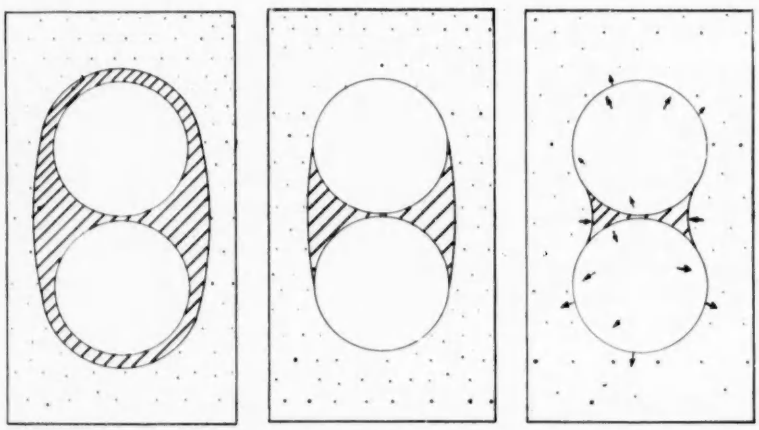


FIG. 5. *Idealized conception of water film enclosing two fibers in the center of a wet fabric:* a—*early in constant rate period;* b—*towards end of constant period;* c—*during falling period. Surrounding atmosphere in* a *and* b, *100% R.H.; in* c, *< 100% R.H.*

state depicted by Figure 5(c) is achieved. This state is believed to correspond to the termination of the constant-rate period and the onset of intrafiber diffusion. At this time the "wet-bulb" temperature of the fabric must begin to rise, and the total rate of energy input for evaporation begins to drop.

Figure 6 illustrates the effect of surface hairiness upon the impedance of the stagnant boundary film of air. When this region shades off, as indicated by Figure 6(a), it can be expected that the barrier effect will be greater than as indicated in Figure 6(b). Water mass and the energy for continued evaporation from the internal liquid films must ultimately be exchanged across this barrier. Since the net rate of energy transmitted across this vapor boundary is considered to be the limiting factor in the mass energy transfer, it is apparent why the constant drying rate of a hairy fabric may be somewhat depressed.

Now, some consideration must be given to the processes by which the lower edge of the boundary film is maintained near saturation as evaporation proceeds. One might postulate a simple concentration gradient to exist wherein as soon as a vapor molecule crosses the barrier to the "great outdoors," a space is made available for another vapor molecule to move in from the reservoir below. The "hole" is thus passed backwards into the atmosphere of the body of the fabric eventually to be occupied by a water molecule which leaves some liquid surface.

No doubt this process is operative. It is suggested, however, that additional conditions probably prevail to promote vapor diffusion from the interior to the exterior of the fabric.

For example, Preston [22, 25] postulated a mechanism for vapor transport whereby heat gradients within a fabric structure induce selective evaporation at one site and recondensation at others, so that a continuous flow of vapor may be going on within a wet textile structure whose internal atmosphere is maintained at 100% R.H. The droplets of alcohol observed near the lip of a cocktail glass which continually run down into the cocktail is an example of this type of gaseous migration induced by temperature differentials within a vapor region of total saturation.

Whether any significant temperature gradients existed within the fabrics as they dried under the conditions of this experiment is not known. However, another type of gradient may have existed which would operate to foster vapor diffusion from the interior towards the exterior of the fabric. The vapor pressure exerted at a convex liquid surface is greater than that of a saturated atmosphere over a flat surface. A concave liquid surface has a partial pressure lower than that of a saturated atmosphere. Therefore, if there exists within the fiber-water matrix two regions, one in which the average fiber-water configuration corresponds to Figure 5c and the other resembling Figure 5a or 5b, there will be preferential diffusion of vapor from the vicinity of the latter towards the former. Thus, fibers immediately adjacent to the fabric boundary surface will not be divested of liquid water much more rapidly than will fibers towards the interior of the fabric.

Aside from vapor-phase transport induced by temperature and concentration effects, there will undoubtedly also be liquid migration within the fabric core. Convection as well as capillary migration are probably both participating in the redistribution of water. According to the present conception, however, liquid migration is not a rate-controlling influence during the constant-rate periods.

The rate-controlling influences from the time of total saturation down to a point somewhat prior to the 100% R.H. equilibrium moisture regain are believed to be those intrinsic fabric geometric factors and extrinsic atmospheric conditions which operate on the vapor film at the periphery of the substrate. If impinging air is increased in velocity, for example,

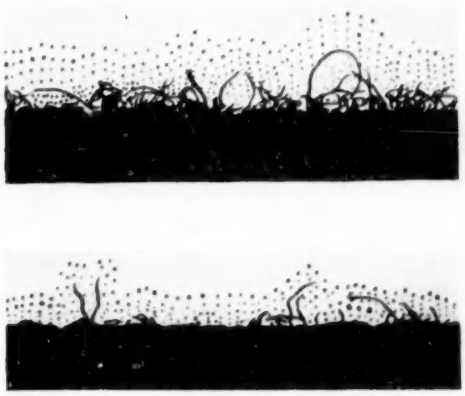


FIG. 6. *Conception of vapor boundary film at surface of hairy fabric* (a) *and relatively smooth fabric* (b). *(Sketched from Harris* et al., TEXTILE RESEARCH JOURNAL **23**, *108 (Feb. 1953).)*

fabrics of greater thickness might show a decrease in rate at a higher fraction of void volume occupied by liquid, since the gross rate of vapor migration to the peripheral boundary will eventually reflect the greater length of travel from the center to the exterior of the fabric. Some other effects of fabric geometry on vapor diffusion through fabrics have been discussed by Gregory [11]. Ultimately for all fabrics, however, the total moisture content approaches the equilibrium regain at 100% R.H., and a new state of affairs may ensue.

Intrafiber Diffusion

The subject of saturation equilibrium moisture regain has received considerable attention in the literature, with some very marked discrepancies reported by various workers. Values of equilibrium moisture regain for wool, for example, have been given as low as 30% and as high as 60% [17]. Such differences cannot be attributed entirely to an exaggerated hysteretic influence at ultimate swellability. It is more likely that the explanation resides in experimental technique and a failure to account for liquid water condensed and retained within a fiber assembly by capillarity. This is not simply a question of inadvertent condensation because of the very precise temperature control required in order to avoid precipitation at 100% R.H.

It has been indicated [24, 25, 26] that approximately 10%–15% by weight of fibers in common structures may be retained in capillaries even after centrifugation, and under vacuum. This is a hydrostatic tension effect, and the amount of water retained by such a mechanism is functional with the capillary volumes as well as their shapes.

It is not the purpose of this work to provide a detailed anaylsis of the role of capillary-retained water upon certain methods of determining fiber equilibrium moisture regain at 100% R.H. (a condition which, by definition, is one of static equilibrium). What is of consequence, however, is the manner in which liquid and vapor transfer during drying may occur. The relationship between fiber equilibrium regain and the tendency for fiber assemblies to retain liquid water is therefore of particular concern during the last stages of liquid evaporation. The possible role of intrafiber diffusion and its effect on the final evaporative stages of drying should be examined.

Vapor transfer from the interior to the exterior of the fabric structure combined with a continual redistribution of liquid by capillary migration under hydrostatic tension and perhaps also by convection are all believed to prevail during the extended constant-rate period observed in this work. It must be remembered that the several concomitant phenomena are involved in an over-all dynamic equilibrium with the net rate of mass-energy exchange through the vapor film boundary. So long as fiber surfaces are wet and liquid films are either concave or flat, the vapor "well" within the body of the fabric is maintained at very near 100% R.H. Eventually, however (as aqueous volume approaches 10% of fiber volume), the retained liquid films will be found in crevices and capillaries with concave menisci.

It will be seen from Figures 7–10 and the data of Table IV that the constant-rate period ends when the total moisture content is significantly in excess of the respective 100% R.H. regain values of the several fibers. Liquid water is still present when the drop in rate starts. The fall progresses smoothly right through the region of total water content that corresponds to 100% R.H. e.m.r. for all of the fabrics except the wools. In the latter instances, there is a consistent indication of a trend towards leveling-off in the evaporation rate at a moisture content somewhere between 55% and 35% regain.

That this arrestation in the evaporation rate decrease is not experimental error or an artifact may be verified by reference to the several figures given by Paul and Wilhelm [20]. It will be seen that all of the wool fabrics employed in the work of these authors exhibited the same type of inflection in the same regain region practically irrespective of the external conditions prevailing during drying. Indications of this effect were also observed by Fisher [7], who wrote: "A re-examination of earlier data up to 125% H_2O with wool fabrics indicates that generally the time curve [our Figure 1] is straight down to about 31%, but that occasionally the experimental points are very irregularly placed between 40 and 30% H_2O content, and in these cases the points are always on the same side of the curve, suggesting that an irregular falling off in rate of evaporation occurs in this region."

The complexity of effects during this period of evaporation (from approximately 50% to approximately 35% regain for wool) may also be inferred from the temperature *versus* regain curves of Paul and Wilhelm [20]. It will be seen that the meas-

ured surface temperature of the fabrics remains constant during both their constant- and first falling-rate periods, but begins to rise at about 55% regain. However, it does not rise smoothly during the subsequent period. In some instances, the graphs indicate decided double inflections, and in others there is first a slow, flat rise in temperature between 55% and 30% regain before a rapid rise to the point of ultimate dryness.

It is not surprising that many workers have failed to note and comment upon the double inflection found in the drying rate *versus* regain curves for wool in the region slightly above fiber saturation moisture regain. When time is plotted against weight, as illustrated by Figure 1 and as employed in the article by Fourt *et al.* [9], a slight flattening of the curvilinear portion of the curve, as indicated at *A* in Figure 1, would likely be missed. It is

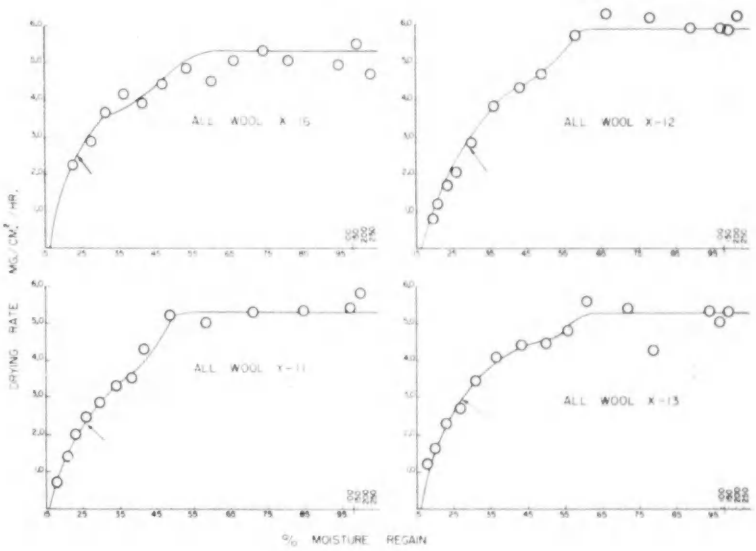


FIG. 7. *Drying rate curves, wool fabrics. (Arrows indicate point of palpable dryness.)*

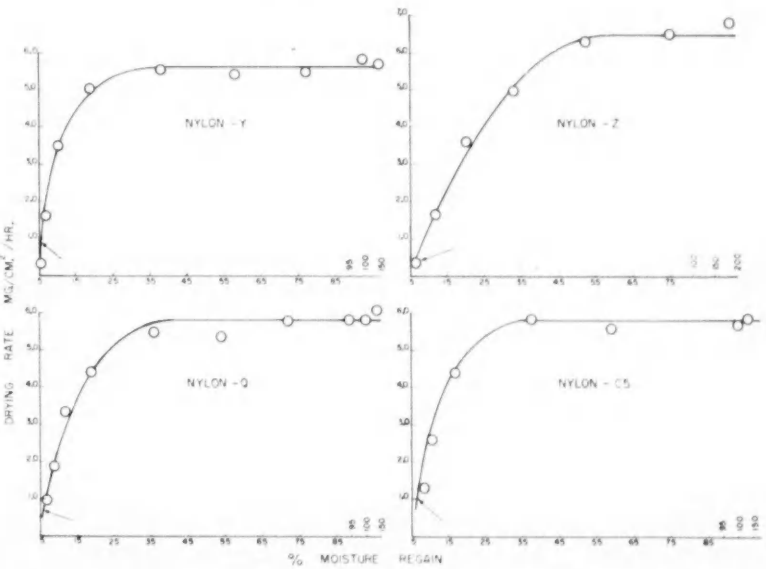


FIG. 8. *Drying rate curves, nylon fabrics. (Arrows indicate point of palpable dryness.)*

gratifying that the very precise experimental technique of Paul and Wilhelm did not neglect to record the resulting inflection in the derivative rate *versus* regain curve. These authors accepted, however, the saturation equilibrium value of about 54% for wool, which is considerably too high. If they had had the benefit of the findings of Preston and coworkers at their disposal, the double inflection exhibited by their plots might not have gone unnoticed by them.

The fact that the arrestation in rate drop occurs for wool and not for the other fibers calls for some explanation. The onset in falling rate is ascribed, for all fabrics, to a change in the thermal balance of the evaporating system. The total internal liquid area rapidly diminishes in the transition between the situations depicted by Figure 5 (b and c). The cooling effect due to internal evaporation is diminished; the heat gradient across the boundary film

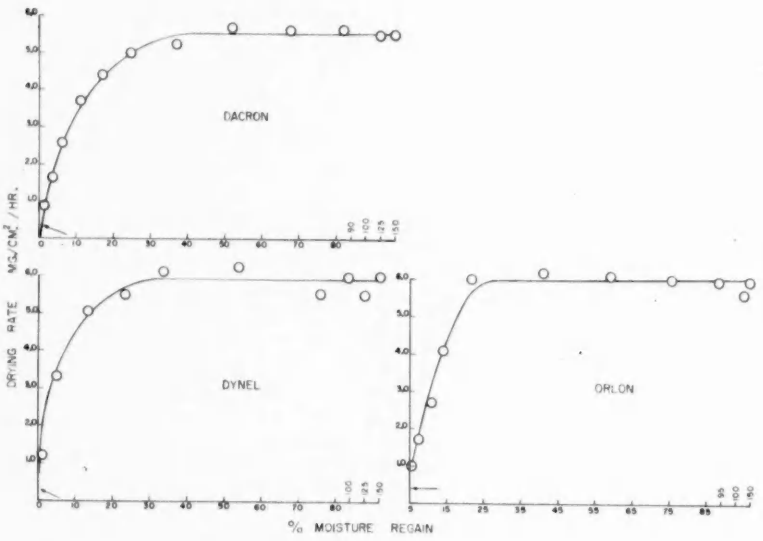


FIG. 9. *Drying rate curves, nonhygroscopic fibers. (Arrows indicate point of palpable dryness.)*

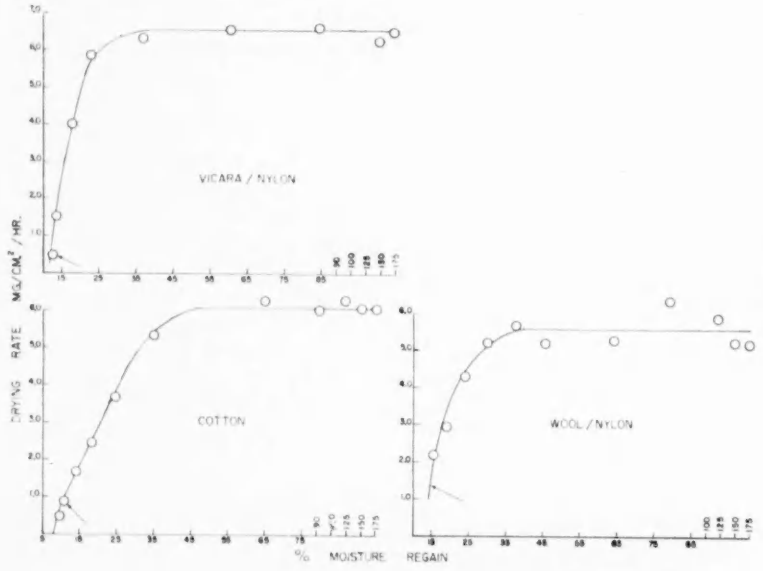


FIG. 10. *Drying rate curves, fiber blends and cotton. (Arrows indicate point of palpable dryness.)*

diminishes; the total rate of energy transmission to the fiber-water assembly decreases. Now, because the residual liquid water is enclosed beneath concave surfaces, the vapor pressure over these liquid films is limited in accordance with the Kelvin equation:

$$\ln p/p_o = \frac{2\gamma M}{r \rho RT}, \qquad (1)$$

where p = vapor pressure over the curved surface, p_o = saturation vapor pressure of a flat surface, γ = surface tension of liquid, M = molecular weight of the vapor surface, r = radius of curvature of the liquid, and ρ = density of liquid.

At the reduced vapor pressure, p, evaporation may occur from fiber surfaces that are water-swollen but otherwise devoid of liquid films. If liquid diffusion to such surfaces is sufficiently rapid, internal evaporation may continue at a high enough rate to arrest the diminishing thermal gradient. If the intrafiber diffusion is too slow, the fabric temperature continues to rise, approaching the ambient temperature continuously as the liquid in capillaries must continue to provide the major source for evaporation, and the over-all mass-energy transfer decelerates. It would be interesting to compare possible rates of intrafiber diffusion with the over-all evaporation rates during the period when liquid water is still present in capillaries.

Analysis of the intrafiber diffusion problem may be treated roughly as diffusion through a film. Doty, Aiken, and Mark [5], Hauser and McLaren [12], and Singleton and Johnson [28] have studied the water vapor permeability of films of nylon, cellophane, acrylonitrile copolymer, and other polymeric materials. Information on the diffusion behavior of wool and horn keratin has been given by King [14, 15, 16], Baxter [1], and Peirce, Rees, and Ogden [21]. An excellent review of the entire subject was written by Newns [19].

TABLE X

A—Diffusion Coefficients of Water in Fibers at 100% R.H.

Fiber	$D \times 10^7$ (cm.²/sec.)	Authority
wool	20, 80, 100	[1, 21, 16]
cotton	6	[1]
nylon	2.5	[12]
acrylonytrile copolymer	<1	[12, 28]

B—Calculated Solubility and Permeability Coefficients

Fiber	$S \times 10^3$ (moles/cc./cm. Hg)	$P \times 10^{10}$ ($S \times D$)
wool	16	320
cotton	12	72
nylon	4	10

The approximate values for diffusion coefficients which are either given by these several workers for 100% R.H. or may be calculated from their data are given in Table X. These are necessarily rough values, useful essentially for the order of magnitude of effects. From other evidence [8, 21], however, it appears that wool is at least ten times more permeable to moisture vapor than is nylon, and about three to four times more permeable than cotton.

According to the experience of Kovacs [18] and Houwink [13], the diffusibility of liquids is very little different from their saturated vapors (including water and water vapor) in a variety of films including cellulose acetate. We may presume, therefore, that the coefficients given in Table X will apply in the present case for diffusion of water through the several different fibers from their surfaces wetted by trapped capillary water to opposite liquid-free surfaces.

The diffusion coefficient, however, simply describes the probability of a molecule of water moving a certain distance in a certain time, under the applied pressure gradient. The over-all transfer, or permeability, P, of moisture through a film depends also upon the amount of water that may be contained in the film at the mean pressure involved; $P = DS$, where D is the diffusion constant and S is the solubility coefficient. S, defined by Henry's Law, should include only water that is ideally dissolved, rather than the total amount, which includes chemically bound water. In any event, an approximation of S for present purposes may be calculated from

$$Sp = c, \qquad (2)$$

where p = vapor pressure of H_2O (cm. Hg), and c = concentration of dissolved water (moles H_2O/cc. fiber).

Values for S given in Table X(B) were calculated in accordance with this equation, using $p = 1.75$ cm. Hg (saturated atmosphere at 20°C), and equilibrium regains for wool, cotton, and nylon taken as 35%, 25%, and 11%, respectively. The permeability constants, P, for the several fibers at saturation

were calculated by $D \times S$, and these are also shown in Table X(B). For wool, the lowest value of D given in Table X(A) was used.

Now, the quantitative transmission of water through a film can be found from

$$\Delta p = \frac{Nl}{PAt}, \qquad (3)$$

where N = number of moles of H_2O, $P = D \times S$ (as previously), A = area of film (cm.^{2}), l = thickness (cm.), t = time (sec.), and Δp = pressure gradient across film (cm. Hg). Assume, now, that the geometry shown in Figure 5(c) is a reasonable depiction of the typical water-fiber assembly during the last stages prior to ultimate fiber desorption. Let us assume the radius of the fiber to be the equivalent of film thickness (of equation (3)), and half of the total fiber periphery to be the area of the film through which diffusion evaporation is to transpire (A of equation (3)). What, then, is the pressure differential required to maintain an evaporation rate of 4 mg./hr./cm.^{2} of fabric (see Figure 7) if *all* of the water to leave the fabric must first diffuse across the fibers from capillary reservoirs of liquid?

Table II indicates there is about 20 cc. of fiber per fabric of 300 cm.^{2} projected area or of 600 cm.^{2} area for evaporation. Allowing the wool fiber average diameter to be 20μ, it can be shown that there will be a total fiber periphery of 60 cm.^{2} per cm.^{2} of exposed fabric surface. Therefore, $l = 10^{-3}$ cm. ($\frac{1}{2}$ of 20μ), $A = 30$ cm.^{2} ($\frac{1}{2}$ of 60 cm.^{2}), $N = 4/1{,}800$ moles (4 mg. H_2O), $t = 3{,}600$ sec. $P = 320 \times 10^{-10}$ moles-cm./cm. Hg/cm.^{2}/sec., and, by substitution in equation (3), $\Delta p = 6.4 \times 10^{-4}$ cm. Hg. Thus, when the relative humidity in the internal atmosphere of the wool fabric specified drops to 99.96% at 20°C, diffusion of water through the fibers from trapped capillaries to nonwetted fiber surfaces will be at a rate sufficient to maintain overall fabric evaporation rate at 4 mg./cm.^{2}/hr. According to Preston [26], capillary water of the order of 10% by volume of fiber may be present in fabrics whose internal atmosphere is 99.97%, while at 99.8% R.H. the retained water would be of the order of 1% of fiber volume.

It appears from a study of these figures that for the possible 10% of liquid water which is trapped in capillaries or under concave surfaces in wool fabrics at 99.97% R.H., access to the atmospheric well is still available by diffusion through the fibers themselves for evaporation. The total permeability is such that the drop in over-all fabric evaporation rate may be arrested temporarily at about 4 mg./cm.^{2}/hr. while the last traces of liquid water are drained from the capillaries.

It can be shown, on the other hand, that for nylon, using a film thickness of 5μ (*i.e.*, a fiber of 10μ diameter) and a film area of 60 cm.^{2}, the same Δp (*i.e.*, 6.4×10^{-4} cm. Hg) would produce a total net permeation rate of only 0.5 mg./cm.^{2}/hr. All of the other fibers, except cotton, can be expected to have even lower intrafiber diffusion capacities. Therefore, the internal evaporation of capillary water in these fabrics must proceed primarily from liquid films which are progressively degenerating both in total area and in vapor pressure. For cotton, it is difficult to approximate film dimensions because of the irregular shape and size of fibers. However, the general shape of the cotton drying curve (Figure 10) seems to indicate a possible discontinuous drop in the region near 25% regain and a level of about 3 mg./cm.^{2}/hr. evaporation rate. This might well be accounted for by the liquid diffusion mechanism postulated for wool.

The Question of Time to Dry

Quantification of a subjective property such as sensation of dryness is rather difficult. Such expressions as "very dry," "half dry," etc., are rather elusive answers to the question "How dry?" For present purposes, the socks were considered to be dry only after they had reached an equivalent condition for all cases. This condition was judged arbitrarily, one must admit, as the state at which the socks could be donned without creating a feeling of dampness, coolness, or clamminess.

It is interesting that the condition described was achieved by all socks at a level equivalent to moisture regain in equilibrium with about 80%–90% R.H. Drying rate had by this time been falling for some time. Certainly the condition of capillary-retained liquid was passed. On the other hand, it is noteworthy that not a great deal of the regain moisture in excess of the 65% R.H. e.m.r. was required to evaporate before the fabrics no longer felt damp. This is not too surprising since fabrics in contact with the body, and therefore in equilibrium with an atmosphere approaching 100% R.H., are not customarily considered damp.

It must be remembered that the results described herein apply to convective air drying in the absence of high external radiant energy sources and at relatively low air velocity. This is a condition which obtains, for example, when a woman rinses her lingerie and hangs it next to her husband's towel on the rack in the bathroom. Some garments will dry in 1 hr., more or less, and some may take overnight to reach a point of palpable dryness. There are many modifications of the possible procedures employed to reduce the length of time to dry. The principal technique, of course, is to relieve the fabric of as much of its retained liquid water as possible.

Figure 11 is a plot of the elapsed time from the condition of towel-drainage to that of palpable dryness. The ordinate is the ratio of total liquid water to surface area of evaporation. There is no trend suggesting that any of the several different fibers are inherently quicker drying. The time to dry is simply proportional to the amount of water to be evaporated per unit area of exposed fabric surface. The amount of water retained has been shown to depend upon the method of extraction, except that certain fiber-controlled fabric properties may promote high uptake and retention due to capillarity.

Table XI gives the time to dry from each of the three conditions: towel-drained, squeezed, and centrifuged in a Bendix machine. The values given in column *A* are experimental, and these are the points plotted in Figure 11; the values given in columns *B* and *C* were calculated using the values of retained water given in Table III and the rate data for drying given throughout. It is difficult to assign practical significance to such differences as are noted.

TABLE XI. TIME TO DRY SOCKS

Code	Fiber	*A* Towel-drained (experimental hrs.)	*B* Squeezed (calculated hrs.)	*C* Bendix (calculated hrs.)
X-12	wool	11	4.5	5.5
X-13	wool	11.5	5.0	5.0
X-14	wool	15	4.0	5.0
X-15	wool	21	7.5	7.5
X-16	wool	12.5	6.5	7.0
Y-11	wool	11.5	—	—
X	nylon	18.5	6.5	6.5
Q	nylon	8.5	5.0	4.5
C-5	nylon	8.5	4.5	5.5
Y	nylon	8.0	5.0	4.5
Z	nylon (fllament)	6.5	—	—
D-1	Orlon	11.0	7.5	7.5
E-6	Dacron	10.0	6.0	6.0
C-2	Dynel	10.0	5.0	7.0
G-4	Vicara/nylon	9.5	5.0	5.5
B-10	wool/nylon	14.5	6.0	7.0
—	cotton	10.5	—	—

The popular conception that some fibers are rapid-drying probably depends upon the fact that these fibers have been found in fabric structures either of low surface impedance or with low ratios of void volume to surface area. When these fibers, however, are spun in loose twists and knitted in bulky and hairy structures, their intrinsic low regain does not favor their drying rate. On the contrary, the actual time to dry such fabrics may well be somewhat increased because of the more thorough saturation of their total void volume, as permitted by the capillary-penetration mechanism described previously.

Summary

1. A variety of fibers in similar knit structures were studied to determine the effect of inherent fiber properties on speed of drying under ordinary household conditions.

2. The major part of the drying cycle from near-saturation down to within 15% regain above 100% R.H. equilibrium moisture regain is characterized by a constancy in evaporation rate. This rate, in grams/centimeter^2/hour, is equal, irrespective of fiber content, except that smooth-surfaced, nonhairy fabrics exhibit somewhat higher rates.

3. Total drying time, under household drying conditions, is dependent upon the ratio of total moisture uptake to peripheral surface area of fabric.

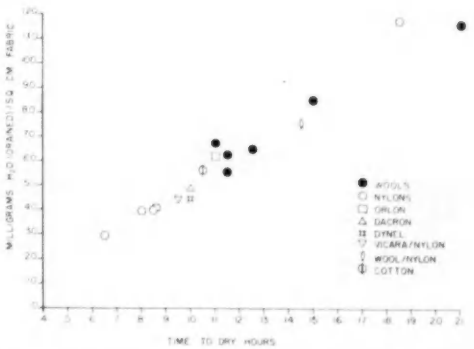


FIG. 11. *Drying time from condition of towel-drainage plotted* versus *ratio of contained water to fabric area.*

4. The drying mechanism is believed to depend upon vapor diffusion from the atmospheric "well" within the fabric to its periphery, and thence through a boundary film, where mass-energy transfer occurs.

5. Towards the end of drying, the water retained in interfiber capillaries is believed to be replenishing the atmospheric "well" by evaporation from both concave liquid films and from saturated fiber surfaces. The total rate of dissipation of this capillary-retained water into the atmospheric "well" may be greater for fibers of high moisture permeability.

6. The fall in over-all evaporation rate begins at about 10%–20% water content above 100% R.H. equilibrium moisture regain for all fabrics. This drop in rate is momentarily checked in the case of wool fabrics before the entire supply of liquid water has evaporated. For other fibers, the fall in rate occurs smoothly without any indication of arrestation.

7. The volume uptake of water at saturation is approximately equal to the void volume of all of the wet fabrics, except in the case of wool. Fiber crimp and surface roughness are believed to impede capillary penetration into all pores of a wool yarn, and thus account for only about 75% void occupation.

8. The rate of capillary migration is shown to be high for the smooth-surfaced fibers and low for wool, with the rate increasing with increasing non-wool content in a series of tropical suiting fabrics.

9. Sensation of "dryness" is achieved at a total moisture content somewhat lower than the 100% R. H. equilibrium moisture regain of the fibers.

Acknowledgment

The author wishes to acknowledge the assistance of Messrs. E. Singer and L. N. Backer in the performance of this work. He also wishes to express his gratitude to Mr. Giles Hopkins, Technical Director of The Wool Bureau, Inc., for his cooperation during the prosecution of this work.

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(*Manuscript received May 7, 1953.*)

Use of the Ballistic Pendulum for Impact Testing of Tirecord

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Abstract

A ballistic pendulum tester for the absolute measurement of the energy (or work) of rupture of cords and yarns on impact is described, and the applied theory of the pendulum is briefly reviewed. Essentially, the test consists of placing a looped specimen, clamped at its ends, in a horizontal plane, so that it is struck in the bend of the loop by the pendulum at the bottom of its swing with sufficient energy to break the specimen. The difference in angular displacement of the pendulum with and without a specimen in place provides the measure of the energy lost in breaking the specimen.

For expressing the results of the test as applied to tirecord, with reference to various conditions, four physical quantities have been defined. The significance of these quantities is discussed, and the results of exploratory tests on a number of rayon constructions are given, showing the application of the various measures.

By means of high-speed photography, used in connection with the pendulum apparatus, the impact rupture process in tirecord has been analyzed, and the energy separated into its force and elongation components. It is revealed that an experimental cord having higher-than-normal strength by the conventional test not only has a lower energy of rupture than a viscose control, but also appears to have lower impact strength. The analysis shows that the "breaking point," even in an impact test, is not an instantaneous phenomenon.

Introduction

A well-known, if not obvious, service requirement of the pneumatic tire, and therefore of its textile structural element, is resistance to rupture under impact loading. The property of strength is involved in establishing the level of resistance in the impact process, but not under conditions which prevail in the usual strength test. The conventional tests of textile materials, including tirecord, are conducted with a relatively low rate of loading, whereas in the impact process the load is applied rapidly. Hence, the breaking load found for a tirecord by conventional means is only remotely related to the agencies in a tire fabric which come into play when it is shock-loaded. It has been well established [2, 4, 6] that the breaking load of yarns or cords varies with the rate of loading, generally increasing with increasing rate. The amount by which the resistance to rupture increases with testing speed may vary among different materials, and, accordingly, the rank of materials with respect to this property may be completely different under impact conditions from what it is in the conventional low-speed tests. Thus, the latter tests may give only inaccurate, if not actually spurious, predictions of the impact performance of such products as tirecords.

A second disadvantage of the conventional test as a means of assessing the mechanical performance of tirecords lies in the emphasis it places on breaking load. As pointed out by Midgley and Peirce [5], the resistance which a material is capable of offering to rupture depends upon the extension it can undergo before rupturing, as well as upon the tensile force which must be applied. A material which could tolerate more extension than another before rupturing, in actual service—in apparel as well as in mechanical textiles—would be regarded as the more serviceable or durable, even though the applied force at the instant the break occurs is the same in the two cases. This basis for the evaluation of resistance to rupture has its quantitative counterpart in the work or energy of rupture—*i.e.*, the integrated product of each infinitesimal strain up to the breaking point and the force producing that strain at the particular instant.

The pendulum used ballistically provides a convenient means for overcoming the aforementioned objections to the conventional tensile test of tirecord.

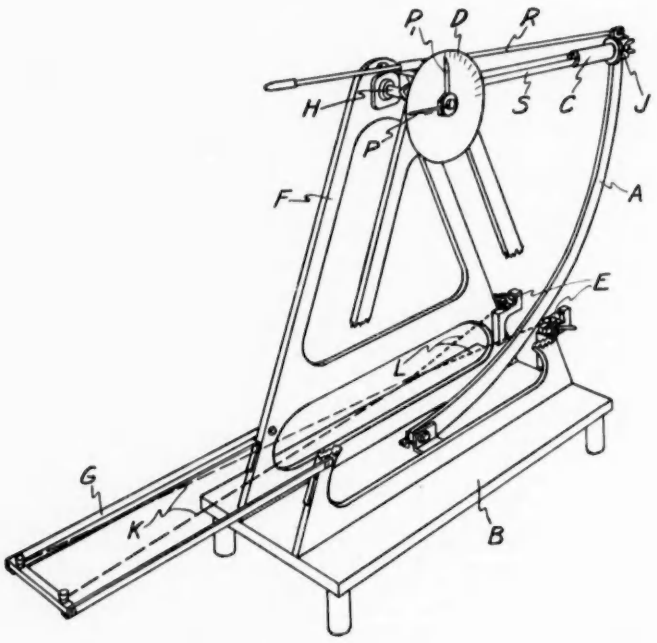

FIG. 1. *Ballistic pendulum apparatus for impact rupture tests on textiles, principally tirecord.*

An extensive description of a ballistic pendulum test was given years ago by Midgley and Peirce [5, 7], although impact tests of this type had been used earlier [1, 3]. The present report concerns a pendulum apparatus resembling that of Midgley and Peirce, but employing what is believed to be a novel method of mounting and rupturing the specimen.

Apparatus and Experimental Method

The impact apparatus is shown in Figure 1. The pendulum proper consists of a cylindrical bob, *C*, 16.5 cm. long, attached to a hollow, square shaft, *S*, 76 cm. long, which in turn is suspended from a horizontal axle, *H*, mounted in self-aligning ball-bearing assemblies. The bearings are supported by two heavy, triangle-shaped uprights, *F*, cut from boiler plate. An arc, *A*, lying in the same vertical plane as the pendulum, just outside the path of the swinging pendulum bob, carries an adjustable pendulum holder, *J*, by means of which the pendulum can be held at any initial deflection up to about 90°. Pivoted at its lower end, the arc is held in place (with the holder *J* against the bob) by means of the approximately horizontal rod *R*. Longitudinal displacement of the rod *R* so as to move the arc outward serves to release the pendulum for its downward swing.

To serve as an angular deflection indicator, a brass disc, *D*, calibrated in degrees of arc (engine-divided), is mounted on the front of the instrument, concentric with the axle *H*, an extension of which passes through the center of the dial. One pointer, *P*, is keyed to the axle, while another, P_1, is held by slight friction to a collar projecting through the brass disc. The latter pointer, which is moved by means of an inward projection on *P*, serves to indicate the maximum deflection or swing of the pendulum after it passes through the equilibrium position.

Mounted in supporting brackets on the right-hand edges of the supporting frames *F*, at about the level of the center of percussion of the pendulum in its equilibrium position, are the cord clamps, *E*, of the conventional snubbing type. Opposite the clamps, on the left-hand side of the instrument, is a light extension member, *G*, to the outer end of which is affixed, by means of binding posts, the cord, *K*, used for aligning the test specimen, *L*, in the path of the pendulum. The scheme for mounting and breaking the test specimen is clearly depicted in Figure 2.*

* Initial trials were made with the cord specimen mounted perpendicular to the plane of the pendulum, in the path of the bob. However, with this method of mounting, the observed individual values were found to be too scattered to be acceptable.

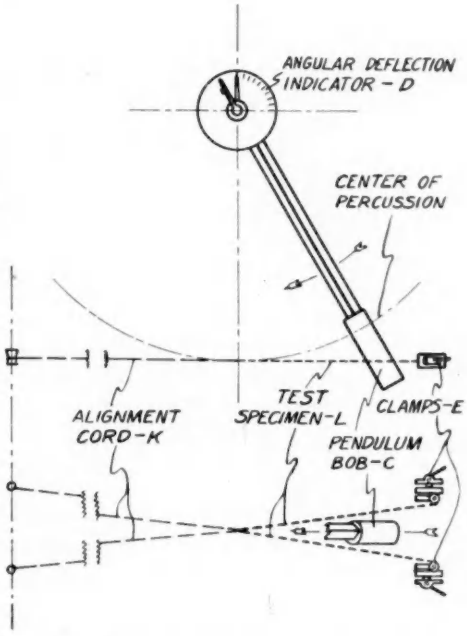

FIG. 2. *Schematic drawing of impact apparatus, showing position of test specimen with reference to pendulum. The brass collar has been omitted from the bob.*

The entire apparatus is mounted on a heavy base, B, equipped with casters to facilitate moving. All parts are of metal, principally steel.

The essential element of the impact apparatus is the pendulum proper. To provide means for altering the radius of percussion, the fixed cylindrical bob is equipped with an adjustable brass collar of 322 g. mass. From the masses and dimensions of the various parts of the pendulum, the distance from the axis of suspension to the center of gravity, X_o, was calculated to be 54.3 cm. (21.4 in.). The moment of inertia, I, was likewise found to be 13.7×10^6 g.-cm.^{2}, while the total pendulum mass, M, is 3215 g.

The radius of gyration, given by the formula

$$K = (I/M)^{1/2} \qquad (1)$$

was found to be 65.3 cm. Finally, the radius of percussion,

$$l = K^2/X_o, \qquad (2)$$

was calculated, 78.5 cm. being found. The cord clamps, E (Figure 1), and the extension member, G, were so positioned on the tester that the test cord when mounted would be struck at the center of percussion as calculated.

The energy absorbed by (or work done upon) a yarn or cord in breaking is given by the relation

$$U = MX_o\, g\, (\cos\theta - \cos\theta_o), \qquad (3)$$

where g is the acceleration of gravity, θ is the angle of deflection of the pendulum from the vertical after rupturing the test specimen, and θ_o is the angle of deflection of the free-falling pendulum without the test specimen. The product $MX_o g$ will be recognized as the first moment of the weight of the pendulum about the axis of suspension. This quantity was measured directly, by weighing the pendulum in a horizontal position (checked by means of a spirit level) at a measured point along its length. It was found that $MX_o g = 1.70 \times 10^8$ dyne-cm., the aforementioned brass collar having been properly positioned. Error due to extraneous frictional losses (bearings, wind-resistance, etc.) has been eliminated from the energy as calculated by equation (3). Only the plausible assumption that these losses are the same with as without a specimen in the apparatus is made.

It has not been found feasible to install a drying chamber on the apparatus, nor to develop a successful technique for quickly removing specimens from an oven and mounting them. Hence, up to the present, all impact measurements have been made on "conditioned" (55% R.H., 75°F) samples.

In practically no case has rupture been found to occur in the segment of the test specimen with which the bob comes into contact. The breaks generally occur in one or the other of the two straight sections of the looped specimen. Occasionally, breaks have been found to occur simultaneously in *both* halves, so that the central section is thrown out ahead of the pendulum. With some samples, the ply yarns of cord specimens have been shattered into a number of short segments.

For the low-speed, so-called "static" tests made in the present experiments, the Scott inclined-plane IP–4 machine, which gives a constant rate of loading, and the constant-rate-of-traverse, X–3 machine were used. The latter provides an elongation rate of 12 in.-min.$^{-1}$

Various Measures of Energy of Rupture

Since the rupture of a yarn or cord involves stretching it along the whole length before the break

occurs, the work involved evidently depends upon the specimen length. To obtain a quantity having more general validity, the energy per unit length of specimen, called the "toughness," * is employed:

$$\text{toughness} = \frac{V}{L} = \frac{MX_o g}{L}(\cos\theta - \cos\theta_o), \quad (4)$$

where L is the total length of the yarn or cord from nip to nip of the clamps. Where a simple measure of the energy of rupture of a textile sample is desired, without reference to other properties, the value given by equation (4) will suffice. In the c.g.s. system, the unit of toughness is the erg-cm.$^{-1}$

To obtain an expression for the toughness of tire fabric prepared from cords being tested, a value, designated the "fabric toughness," may be calculated by multiplying the cord toughness by the number of cords per centimeter of fabric. In this case the unit is the erg-cm.$^{-2}$

For the toughness of a cord relative to its strength, a value designated as the "strength-relative toughness" has been adopted. It is calculated by dividing the cord toughness by the breaking load as measured on a conventional low-speed tirecord tester, the unit being the erg-cm.$^{-1}$-dyne^{-1}.

It may be desirable to express the toughness with reference to unit linear density, and thus obtain a measure characteristic of the material itself, independent of the amount of fiber present in the particular sample. This value, designated the "toughness index," is obtained by dividing the toughness by the linear density (in denier) of the sample. The unit is erg-cm.$^{-1}$-den.$^{-1}$, or dyne-den.$^{-1}$

Experience gained in the testing of conventional tirecord indicated that, for this class of textiles, measurements could be made conveniently with a uniform value of $\theta_o = 85°$, the pendulum being loaded as described above. It was noted further that all of the various expressions for energy of rupture involve cord toughness. Thus, to expedite calculations, a table was prepared, giving values of cord toughness for each 0.5° increment of θ for a uniform specimen length of 100 cm. Evidently, for extensive testing of other types of textile samples, involving changes in pendulum parameters, similar tables could advantageously be constructed.

Typical Experimental Results

The performance of the ballistic pendulum apparatus, used according to regular procedures, can be demonstrated by results of an early test of a series of tirecords. Twenty specimens of each sample were ruptured.

The results on the entire series, including those of low-speed tests using an inclined-plane machine (Scott IP-4), are given in Table I. The fabric toughness values are based on assumed average number of cords per unit width of fabric. If this cord count is that of the fabric before tire building, the fabric toughness of the plies at the crown of a tire, for instance, would be less than the tabulated value, because in the expansion of the tire during manufacture the cord count in this area is reduced.

By way of comparison with the impact results, values are given in Table I for cord toughness under conventional low-speed conditions. As indicated

* The adoption herein of the term "toughness" to denote the work or energy of rupture is in line with textile engineering practice [8]. "Toughness index," similarly, follows the accepted definition.

TABLE I. CONVENTIONAL TENSILE AND IMPACT TOUGHNESS PROPERTIES OF TIRECORDS (55% R.H., 75°F)

Description of cord sample			Conventional low-speed results*					Pendulum impact results			
Material	Construction	Linear density (den.)	Breaking load (conditioned) (lbs.)	Breaking load (conditioned) (10^6 dynes)	Elongation at break (%)	Cord toughness (10^6 erg-cm.$^{-1}$)	Toughness index (10^6 erg-cm.$^{-1}$-den.$^{-1}$)	Cord toughness (10^6 erg-cm.$^{-1}$)	Fabric toughness (10^6 erg-cm.$^{-2}$)	Strength-relative toughness (erg-cm.$^{-1}$-dyne^{-1})	Toughness index (erg-cm.$^{-1}$-den.$^{-1}$)
Rayon (supplier *A*)	1650/2	3673	22.0	9.8	15.3	0.810	221	0.850	8.70	0.0936	231
Rayon (supplier *A*)	1100/2/2	4823	30.6	13.6	13.3	1.034	214	1.303	11.80	0.0994	270
Rayon (supplier *B*)	1650/2	3945	20.8	9.2	16.0	0.752	191	0.886	9.17	0.1120	227
Rayon (supplier *B*)	275/4/3	4150	22.7	10.1	17.3	0.969	233	1.090	11.15	0.1298	264
Nylon	210/4/2	1833	26.0	11.6	20.3	0.969	529	1.260	14.87	0.1132	687

* Obtained on Type IP-4 Machine, Scott Testers, Inc.

above, the work of rupture is, analytically, the integrated product of the stress (load) and the strain (elongation) of the test specimen during the rupturing process. Accordingly, the low-speed values were obtained by measurement of the areas under the load-elongation curves on the tensilgrams.

The toughness index values clearly reveal the intrinsic superiority of nylon in resisting rupture. Thus, on reducing the values to unit linear density (as is done in computing the toughness index), one finds that the nylon possesses three times the toughness of rayon in the conventional tirecord construction. An interesting feature of the strength-relative toughness values, however, is the finding that two of the rayon cords are at least as "tough," in proportion to their conditioned strength, as is the nylon. In other words, the present findings show that the impact-break resistance of nylon cord is, on the whole, not greatly superior to what would be expected from its conventional strength or tenacity.

For three of the samples listed in Table I, histograms have been constructed to show the distribution of individual cord toughness values. They are reproduced in Figure 3. To obtain a further evaluation of uniformity, the coefficients of variation of the impact cord toughness values were calculated from the original data. These are given in Table II.

From data on a number of cord samples, including the five discussed herein, the average standard error in the mean of impact toughness values, for twenty breaks on each sample, was found to be 1.25%. For significance at the 95% level ($t = 2.02$ approximately) this degree of uniformity requires a confidence (or fiducial) interval on the order of $\pm 3.4\%$. As a further test of the actual sensitivity of the technique, the t-value of the smallest cord toughness difference in Table I (that between the two 1650/2 cords) was calculated. The result, $t = 2.905$, indicates that even this small difference is significant at the 99% level.

TABLE II. UNIFORMITY OF CORD TOUGHNESS VALUES OBTAINED IN PENDULUM IMPACT TEST

Sample	Coefficient of variation (%)
Rayon, supplier *A*, 1650/2	4.6
Rayon, supplier *A*, 1100/2/2	6.8
Rayon, supplier *B*, 1650/2	4.3
Rayon, supplier *B*, 275/4/3	2.6
Nylon, 210/4/2	7.7

In Figure 4 is shown graphically the correlation of the toughness indices obtained in the impact test with those from the conventional low-speed tests, for the rayon cords discussed above as well as for other types. No agreement is apparent between the trends of the low-speed and the impact indices for cords of a single fiber type, although there is rough agreement when all types are considered. The mean of the low-speed (IP-4) values for the rayons is about four-fifths that of the impact values. Shown as a broken line is the locus of equal low-speed and impact values. The location of a point below this line signifies that the impact toughness index of the corresponding sample is larger than the low-speed index. For samples having similar elongation characteristics this would indicate that breaking strength (or tenacity) increases with an increase in breaking speed. This tendency was noted previously among textiles of a particular class [2], but it is by no means a general law, as shown below. The dispersion of points in localized regions of Figure 4 is indicative of the need for impact testing in the complete laboratory evaluation of new textile materials, particularly those destined for mechanical application.

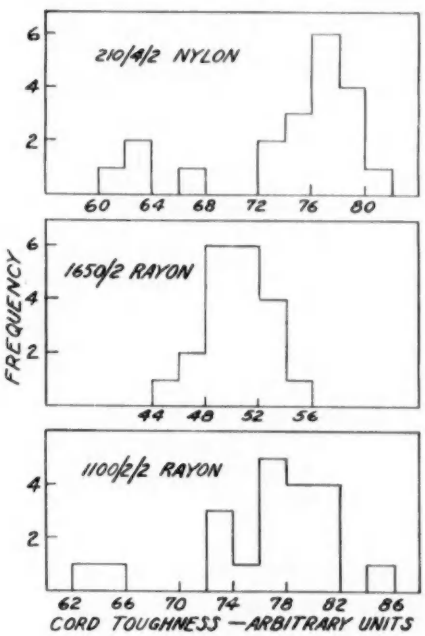

FIG. 3. *Distributions of cord toughness observations on pendulum impact tests for 20 breaks each on three samples. One arbitrary unit* $= 1.696 \times 10^4$ *ergs/cm.*

Analysis of the Impact Rupture Process

In a comparison of pendulum impact values for the energy of rupture with low-speed (conventional cord tester) values of various cellulosic tirecords, it was found that for two cord samples of an experimental material the low-speed values were up to 35% higher than the impact values, while for all-viscose (*e.g.*, Figure 4) and even Fiberglas cords the impact values were found to be higher. Only nylon, in an entirely different range of toughness, had previously been found to behave anomalously. Furthermore, the experimental cords had exceptionally high conventional strengths, while their rupture energies were below those of standard viscose cords. It was recognized that this reduction in rupture energy necessarily represented a reduction in either the impact strength or the elongation, or both. The question was of considerable interest, because if the strength were suffering a loss under impact conditions, the imposing conventional strength of the experimental cords would be of dubious value in mechanical applications.

Analysis of the problem readily disclosed that a fair solution could be obtained if a measurement of the elongation of the sample at rupture could be made, or, better still, if the loading force acting on the cord, as well as the elongation, during the rupturing process could be determined. A time record of the position of the pendulum during the rupturing process would provide the basic information. It was recognized that high-speed photography might provide such a record, and, accordingly, it was decided to try this method.

A black-on-white scale, graduated in 0.1 in. (0.254 cm.), was set up on the impact apparatus at the level of the pendulum bob as it approached, broke, and left the test specimen. A pointer, so arranged as to traverse the face of the scale, was affixed to the bob. The brass collar was removed from the bob for this experiment. An Eastman high-speed camera was set up to view the scale at such a distance that the scale approximately filled the width of a frame.

Photographs of three cord rupture processes on samples of 1650/2 construction were taken. Two of these, one for a specimen of the experimental textile and one for a viscose rayon cord used as a control, proved to provide excellent records of pendulum movement during the rupture process. For these two films the camera was operating (in the critical region) at 2,940 and 3,160 frames/sec., respectively.

By means of a microfilm reader, scale and pointer

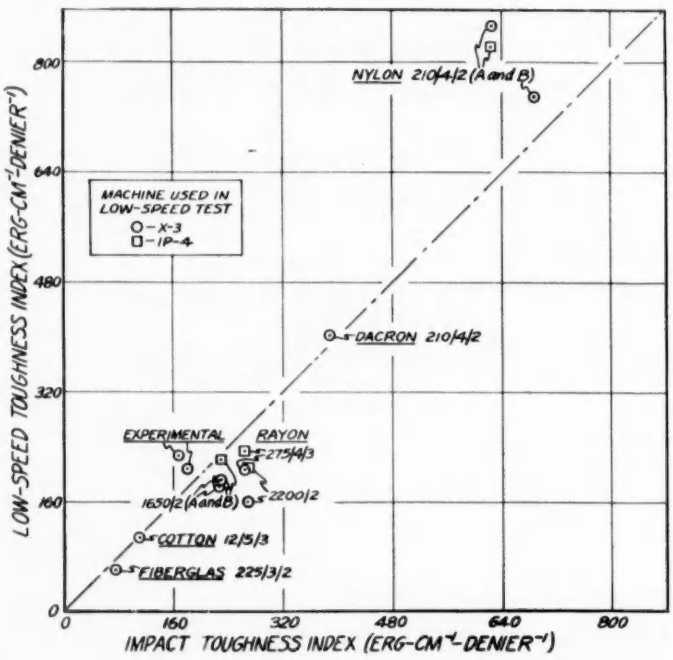

FIG. 4. *Correlation of toughness indices (energy of rupture): impact vs. low-speed measurements for various tirecords.*

readings were taken from the film, frame by frame. The readings were then plotted on a frame *vs.* distance graph. Both film records gave, for the initial stage, a linear relationship between time (as measured by number of frames) and distance, indicating that the pendulum had not yet reached the cord. This section of the graph was followed by one of downward curvature, representing the deceleration of the pendulum as it broke the cord. The final section of the graph was again linear, as the pendulum bob moved away from the broken cord.

An enlarged plot of the curved section of each graph was next made, and on this, slopes at every 2.5 frames were read. The results of these readings were, in turn, plotted on a frame *vs.* velocity (in./frame) graph, and a smooth curve of best fit was drawn through the plotted points. Finally, slopes were read on this graph, giving a relationship between deceleration and frames. The deceleration, at this stage, was conveniently expressed in 0.0005 in./frame^2. Instead of plotting the deceleration data against frame numbers, however, recourse was taken to the initial plots relating distance with frame number. Thus, it was possible to plot deceleration as a function of distance of pendulum travel (or cord elongation).

Using the known speeds of the films, the expressions for maximum deceleration were readily converted to cm./sec.^{2}, and these, in turn, converted to angular measure by dividing by the radius of oscillation (93.1 cm.) of the pointer on the pendulum bob. The torque of the breaking cord exerted on the pendulum so as to decelerate it is given by the relation.

$$T = I_p \alpha, \tag{5}$$

where I_p is the moment of inertia of the pendulum without the brass disk on the bob (11.1×10^6 g.-cm.^{2}), and α is the angular acceleration (or deceleration). The decelerating force, or force with which the cord is progressively loaded during the rupture process, is given by

$$F = T/d, \tag{6}$$

where d is the distance of the impact point on the bob from the axis of suspension (78.5 cm.). By means of these considerations, it is possible to interpret the deceleration as loading force, remembering that this force is divided between the two halves of the test cord on either side of the pendulum bob.* Copies of the loading force *vs.* elongation curves so derived are shown in Figure 5. In the original work sheets, each curve was on a separate graph. The

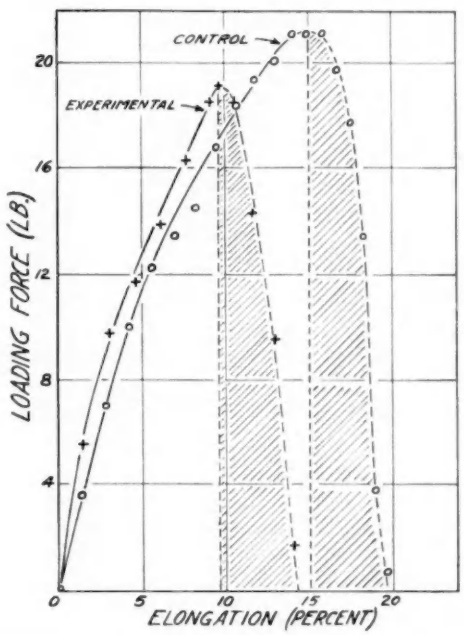

FIG. 5. *Impact rupture curves derived from analysis of high-speed photographs; 1650/2 cords, at 75°F and 55% R.H.*

* Initial velocities of impact of the bob on the cords, on computation, were found to be about 380 cm./sec. ($\approx$ 9000 in./min.).

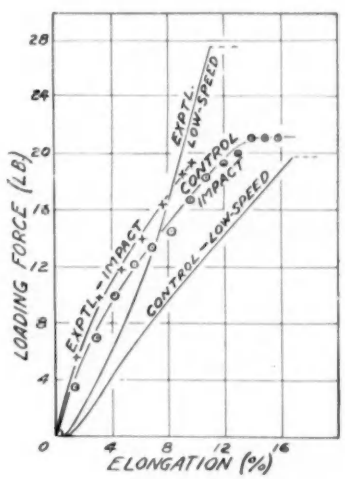

FIG. 6. *Comparison of impact and low-speed breaking tests. Low-speed curves were obtained on a constant-rate-of-traverse machine (Scott X-3 tester).*

loading force, while derived in c.g.s. units, is expressed in lbs. in Figure 5 in order to comply with usage in tirecord technology.

Discussion of Analysis

Figure 5 shows that not only is the elongation (which was the quantity originally sought) obtainable by this photographic technique, but also a measure of an approximate or relative breaking load. A comparison may be made with the results of conventional low-speed breaking tests on the same specimens if the maxima of the curves in Figure 5 are taken as "impact breaking loads." These maxima would seem to correspond to the "breaking loads" registered in the low-speed test. Such a comparison is made graphically in Figure 6. Thus it is disclosed that the impact strength of the experimental cord is distinctly lower than its low-speed strength, while for the viscose rayon control the converse is true.

Not so readily made from Figure.6 is the comparison, within each sample, between the area under the low-speed curve with that under the impact curve.* This area measures the energy of rupture. Cursory examination of either Figure 5 or Figure 6, however, discloses that the area under the curve for the impact test on the control cord is larger than that for the experimental cord, in agreement with the aforementioned rupture energy values obtained from regular dial readings on the pendulum apparatus.

To secure a better estimate of this agreement, planimeter measurements were made on the originals of the curves in Figure 5. The energy equivalent of unit area having been determined, the areas under the curves up to the maxima (initial breaking points), as well as to the end-points, were converted to energy values. The results are assembled in Table III, along with comparable values based on dial readings of the pendulum swing. As indicated in a foregoing section, "impact cord toughness" is the energy of rupture of one centimeter of cord. The values listed as "specific" are those obtained for single specimens from dial readings made simultaneously with the high-speed photographs, while the "average" values are each based on ten impact breaks on the same samples. The two sets of data differ in experimental conditions only in that the brass collar was removed for the photographic experiments. This alteration was, of course, taken into consideration in calculating energy values.

The significance of the dashed-line portions of the curves and the underlying shaded areas in Figure 5 deserves consideration. Evidently, this portion represents the actual cord-breaking process, during which the force resisting the movement of the pendulum drops to zero, as individual filaments break, and the section of the cord remaining across the front of the bob is pushed out of the path. Rupture commences at the peak, but does not occur instantaneously (as would be represented by the vertically descending line in Figure 5). It is, however, of short duration. The times consumed by the descending portions of the curves have been found to be about as follows: experimental (20 frames), 0.006 sec.; control (30 frames), 0.01 sec.

Whatever the mechanism by which the cords are ruptured, the energy represented by the total area under a loading force *vs.* elongation curve is lost by the pendulum. As this is also the energy which is derived from dial readings, the values from the two sources should be in agreement. The agreement on this basis, as shown by Table III, would not at first sight be regarded as impressive. However, it should be recalled that the curves of Figure 5 were derived by the measurement of slopes of curves which are themselves the best fits to plots of prior measurements of slopes. Such a process presents good opportunity for the introduction of error.

By analogy with the corresponding calculations in a low-speed test, the work of rupture would be given by the unshaded areas in Figure 5. As Table III shows, values so obtained agree perfectly with

* Actual area measurements made on the original charts show the low-speed toughness values to be as follows: 0.754×10^6 ergs/cm. for the control, and 0.836×10^6 ergs/cm. for the experimental cord. Comparison with values in Table III indicates that the impact values in Figure 6 confirm the earlier finding that in the experimental cord the impact is less than the low-speed value, contrasting with the relationship for the control.

TABLE III. IMPACT CORD TOUGHNESS (10^6 ERGS/CM.) OF CONDITIONED 1650/2 CORDS

	From dial readings		By photographic method	
Sample	Average	Specific	To break	Total
Viscose rayon control	0.96	0.91	0.91	1.2
Experimental	0.62	0.51	0.51	0.75
Ratio $\frac{\text{experimental}}{\text{control}}$	0.64	0.56	0.56	0.60

those based on dial readings obtained simultaneously. However, no rational justification—*i.e.*, not taking recourse to computational error—can be found for ignoring the shaded areas. The portions of the curves defining these areas represent the continued deceleration of the pendulum, but at a declining rate. This corresponds to the decline of the resisting force to zero. While the force remains greater than zero, however, energy is being expended by the pendulum, and should be represented by an area on a force-elongation graph.

Considering the striking differences between the two methods (high-speed photographs *vs.* dial readings) by which rupture energy (toughness) has been computed, and the possibility for cumulative error in the photographic method, not much better than "order-of-magnitude" agreement could be expected. It is gratifying to find that the agreement is within limits of about 40%. It is conceivable that with the acquisition of experience in the derivation of such curves as those of Figure 5, methods of adjustment could be found so as to give better agreement with dial reading values.

The absence of vertical descents from the maxima of the curves in Figure 5 suggests a certain arbitrariness in selecting a maximal value or reading as the "breaking force" or "strength." Evidently, as the rupture process goes on, the force which is effecting the rupture drops to zero. It is not the maximum, however, but rather some intermediate value which is most representative of the declining force actually prevailing during the rupture process.

Acknowledgments

The authors wish to record the cooperation and interest of G. L. Hall and F. S. Conant, who adjusted and operated the camera in the photographic experiment. The authors are grateful to the Firestone research management for facilitating this research and its publication.

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Note: Additional literature references on impact testing, though not on the subject of tirecords, or the pendulum type of tester, are given in a recent article by H. F. Schiefer, W. D. Appel, J. F. Krasny, and G. G. Richey, TEXTILE RESEARCH JOURNAL **23**, 489 (1953).

(*Manuscript received May 28, 1953.*)

Effects of Construction and Fiber Type on Two-Dimensional Stress-Strain Properties of Fabrics*

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A PREVIOUS PAPER § described the construction and operation of a device to measure the force-extension behavior of a fabric subjected simultaneously to a pair of mutually perpendicular strains. The reason for developing this two-dimensional tester was to provide a more adequate means for predicting the behavior of fabrics in actual use from the results of laboratory tests. Preliminary results were given to afford a comparison between results obtained with this test and with conventional one-dimensional tests. The present paper gives the

* This paper represents a part of the thesis to be submitted by H. K. Woo in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Princeton University.

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§ Reichardt, C. H., Woo, H. K., and Montgomery, D. J., TEXTILE RESEARCH JOURNAL **23**, 424 (1953).

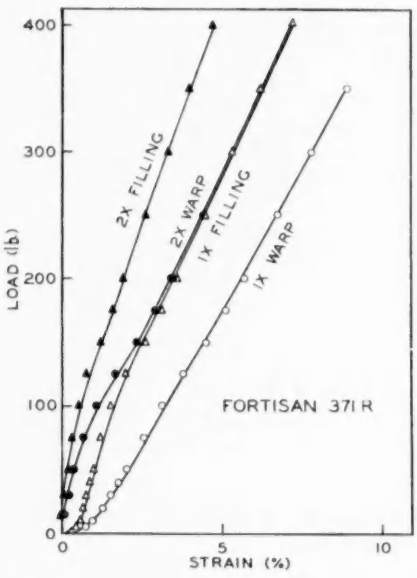

FIG. 1a. *Dependence of load on one-dimensional (1×) and two-dimensional (2×) strain for fabric sample Fortisan 371R.*

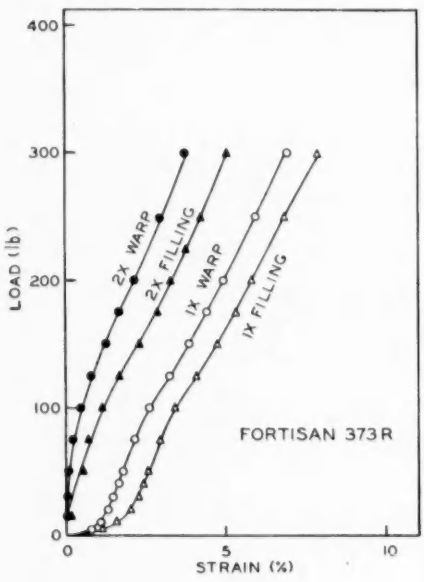

FIG. 1b. *Dependence of load on one-dimensional (1×) and two-dimensional (2×) strain for fabric sample Fortisan 373R.*

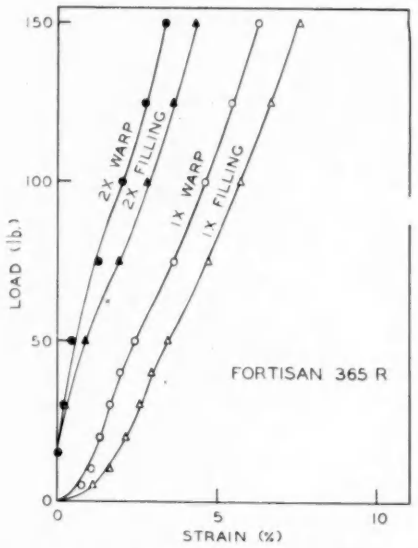

FIG. 1c. *Dependence of load on one-dimensional (1×) and two-dimensional (2×) strain for fabric sample Fortisan 365R.*

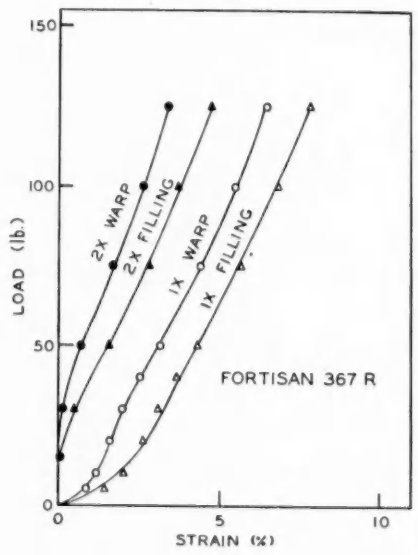

FIG. 1d. *Dependence of load on one-dimensional (1×) and two-dimensional (2×) strain for fabric sample Fortisan 367R.*

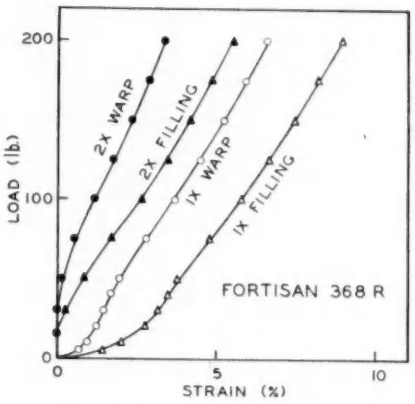

FIG. 1e. *Dependence of load on one-dimensional (1×) and two-dimensional (2×) strain for fabric sample Fortisan 368R.*

results of some experiments to show the effects of construction and type of fiber on the two-dimensional behavior of fabrics. In addition, the effect of coating was investigated by the study of a neoprene-coated airship fabric.

Experimental Results

The apparatus and the method of test were described in the previous paper. The materials chosen for the present tests were as follows:

Set 1 (Effect of Construction)

Weave and cloth analysis:

Sample	Weave	Thread count	Yarn denier Warp	Yarn denier Filling	Fabric weight (oz./yd.²)
371R	2 × 2 basket	2(60 × 26)	60/2	60/5	3.90
373R	2 × 2 basket	2(38 × 38)	90/2	90/2	3.45
365R	twill	100 × 100	60/1	60/1	1.60
367R	plain	100 × 84	50/1	60/1	1.30
368R	twill	96 × 96	90/1	90/1	2.20

Fiber: Fortisan

Set 2 (Effect of Fiber Type)

Weave and cloth analysis: plain weave; thread count 23 × 19

Fibers: cotton, Dacron, nylon

Set 3 (Effect of Coating)

Weave and cloth analysis: sample 373R (of set *1*)

Fiber: Fortisan

Coating: neoprene, 6 oz./sq. yd.

Figures 1a–1e show the results of one-dimensional and two-dimensional tests on the fabrics of set *1*. Here load is plotted as a function of strain. As in the preliminary results given in the previous paper, there is considerable difference between the one-dimensional and two-dimensional tests, the fabrics appearing stiffer in the two-dimensional tests because of the cross-straining effect. Figures 2a–2c show corresponding results for the fabrics of set *2*, and Figure 3 those for the coated fabric of set *3*. For sets *1* and *2*, the average behavior of five specimens for each sample is shown. For set *3*, the behavior of a single specimen is shown.

Discussion

The two-dimensional tests offer a possibility of estimating the difference in behavior between the warp and filling under simultaneous strain. As a convenient parameter to characterize this difference, we shall introduce the asymmetry index α, defined as

$$\alpha = 10 \log |(\text{warp load})/(\text{filling load})| \quad (1)$$

at fixed ϵ, where ϵ is the two-dimensional strain within the uniformly stretched central portion of the specimen. This index is intended to be a measure of fabric imbalance. For a warp load equal to, greater than, or less than the filling load at given two-dimensional strain ϵ, α is zero, positive, or negative, respectively. As a numerical example, if the ratio of warp load to filling load is *2*, at some given strain, the asymmetry index is approximately +3. A similar asymmetry index β can, of course, also be defined with the ratio of loads at a fixed one-dimensional strain. But it will have no direct physical significance unless some theoretical or empirical relationship with α can be established. We have looked at β for some of the fabrics considered here and found that its relationship with α is not simple.

Figure 4 shows the asymmetry index α as a function of two-dimensional strain, ϵ, for fabrics of set *1*. For samples 368R, 373R, 367R, and 365R, it is seen that the asymmetry index α is positive, indicating that with ordinary fabrics where the same yarns are used in the warp and the filling, the warpwise tension exerted in processing has made the warp yarns less extensible than the filling. However, for the construction of sample 371R, the asymmetry index is negative. The physical explanation for this negative asymmetry can be found in the cloth-analysis table for fabric 371R—namely, the filling yarns are $2\frac{1}{2}$ times heavier than the warp ends. This change of sign between constructions suggests strongly that by suitable choice of filling and warp yarns, together with proper control of tension in

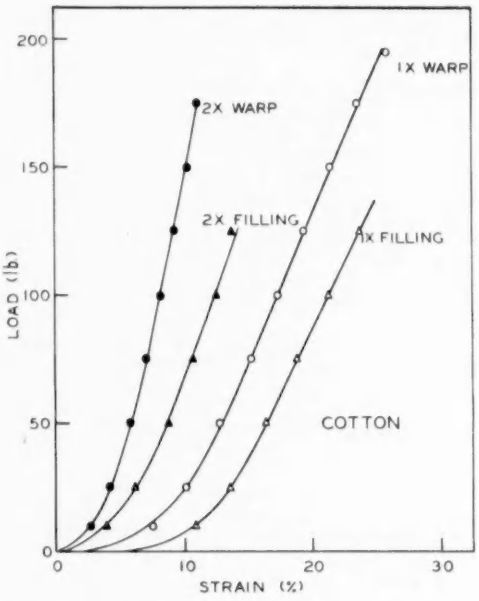

FIG. 2a. *Dependence of load on one-dimensional (1×) and two-dimensional (2×) strain for cotton fabric.*

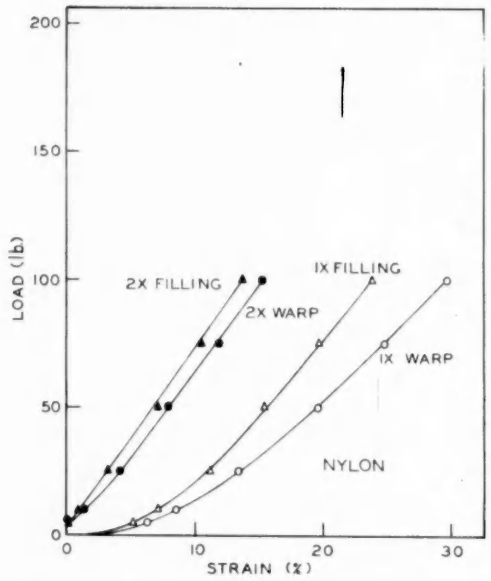

FIG. 2c. *Dependence of load on one-dimensional (1×) and two-dimensional (2×) strain for nylon fabric.*

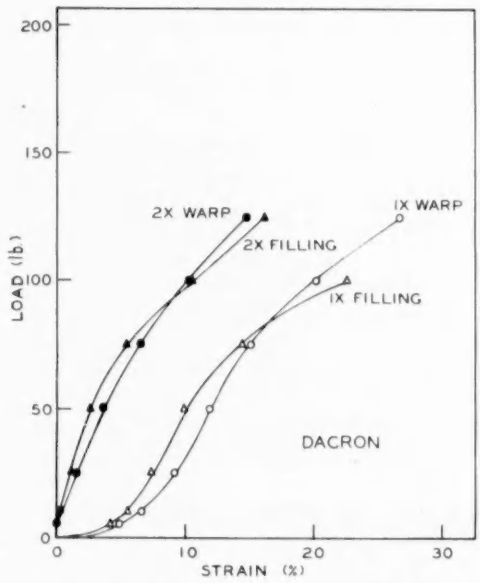

FIG. 2b. *Dependence of load on one-dimensional (1×) and two-dimensional (2×) strain for Dacron fabric.*

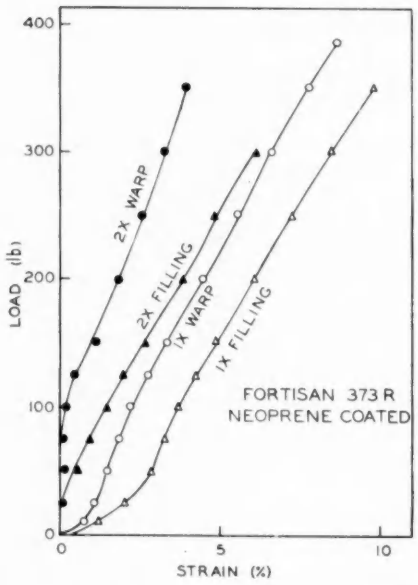

FIG. 3. *Dependence of load on one-dimensional (1×) and two-dimensional (2×) strain for fabric sample Fortisan 373R, neoprene-coated.*

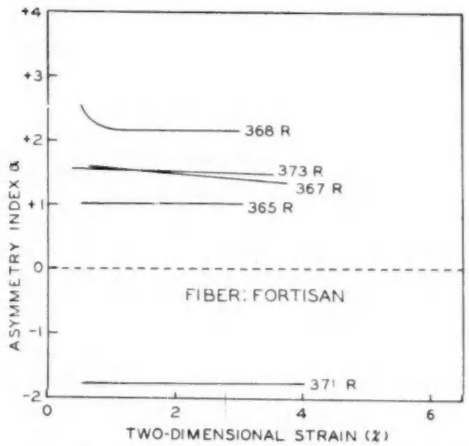

FIG. 4. *Dependence of asymmetry index on two-dimensional strain for fabrics of the same fiber but of different constructions.*

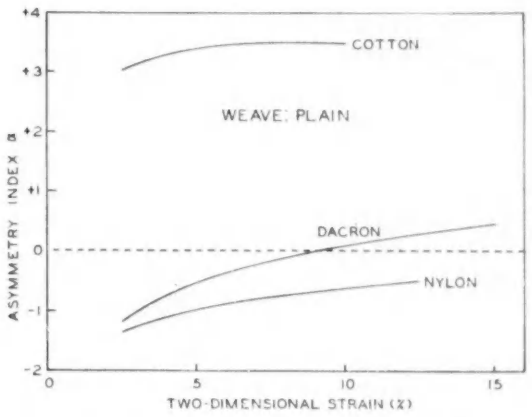

FIG. 5. *Dependence of asymmetry index on two-dimensional strain for fabrics of the same construction but of different fibers.*

weaving and finishing, it would be possible to make a cloth with asymmetry index very close to zero, and thus to obtain a fabric which is very well balanced with respect to extension in different directions under two-dimensional loading.

Figure 5 shows the asymmetry index α as a function of two-dimensional strain, ϵ, for the fabrics of set *2*. For the specified construction of these fabrics, nylon and Dacron show very little load-imbalance, whereas cotton gives a rather high value for α. A plausible reason is that the relatively lower stiffness of nylon and Dacron allows a favorable crimp exchange to take place during cross-straining, whereas cotton, being much stiffer, is incapable of such adjustment. Dacron shows a crossing-over from negative to positive at a two-dimensional strain of about 9%. This behavior is also observed in the one-dimensional tests.

Figure 6 shows asymmetry index α as a function of two-dimensional strain, ϵ, for the coated fabric of set *3*, together with the curve for the untreated fabric. Rather surprisingly, it is seen that the asymmetry for the coated fabric is *greater* than that for the uncoated fabric. It is believed that in applying the coating an excess warpwise tension must have been introduced, making the warp yarns less extensible than in the uncoated fabric. Although we cannot say that this increase in asymmetry is a general result of the coating process, it may be important in explaining the performance of airship fabrics.

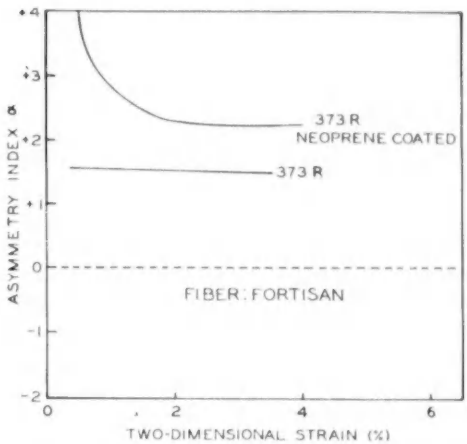

FIG. 6. *Dependence of asymmetry index on two-dimensional strain for neoprene-coated and uncoated fabrics.*

Acknowledgment

We are indebted to Dr. J. H. Dillon and Dr. J. H. Wakelin of Textile Research Institute for their continued encouragement and advice; to Mr. G. D. Mallory of The Goodyear Tire & Rubber Co. for making available to us fabric samples of sets *1* and *3*; to Mr. E. A. McMaster of the U. S. Rubber Co. for the special fabric samples of set *2*; and to Mr. H. W. Lambert of Textile Research Institute for aid in the design and construction of the apparatus.

(Manuscript received July 30, 1953.)

Polymerization of *beta*-Propiolactone in Wool*

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Abstract

The reaction of propiolactone with wool has been studied with the purpose of increasing the rate of reaction within the fiber, while still retaining the enhanced felting qualities of the modified wool. It was found that the presence of water in low concentration, added either to the wool or to the propiolactone in carbon tetrachloride, greatly accelerated this reaction. Excess water reduced the reaction, presumably because of lactone hydrolysis. Addition of water to the system also accelerated the reaction when ethyl, *n*-amyl, oleyl, or dodecyl alcohol was used as solvent, but not when methyl alcohol was thus employed. Significantly, the maximum rate of modification in a mixture of water and amyl, oleyl, or dodecyl alcohol was 30% greater than the maximum with water and carbon tetrachloride. Propiolactone reacts slowly with wool in methyl or ethyl alcohol in the absence of water, but with the higher alcohols, as with carbon tetrachloride, little or no reaction occurs unless water or methyl alcohol is present.

The influence of water and the lower alcohols in promoting interaction of propiolactone within the fiber appears to be the result primarily of swelling of the fiber structure to permit penetration by the propiolactone. In the presence of water the higher alcohols, amyl and dodecyl, can penetrate to cause further swelling and increase in the rate of modification within the fiber.

THE chemical modification of wool by propiolactone to improve fiber felting was described by Jones and Lundgren [4]. The reaction of wool with propiolactone appears to be an anchored, or graft, polymerization, initiated by reaction of propiolactone with certain active sites within and on the wool fiber, particularly amino and hydroxyl groups. Propagation probably occurs through the reaction of propiolactone with the hydroxyl group of the resulting *beta*-hydroxypropionic ester, although this mechanism has not been established. If sufficient time is allowed, polymer formation continues until essentially all of the propiolactone is polymerized. It appears that unanchored propiolactone polymer is also formed, especially when the amount of lactone is higher than 50% to 60% of the weight of the wool, since some of the polymer is extracted by hot acetone or by prolonged extraction with boiling water.

The principal objective of this study has been to examine the conditions which determine the rate of uptake of propiolactone within the fiber, in order to reduce the time required to modify the wool to attain maximum improvement in felting quality. This maximum is achieved when the propiolactone uptake amounts to 50% to 70% of the weight of the wool. Jones and Lundgren [4] found that wool conditioned at 21°C and 65% R.H. (containing about 12.5% of water) reacted very slowly with propiolactone in carbon tetrachloride, but that pretreatment of the wool with ethyl alcohol, or consecutive pretreatment with alcohol, benzene, and ether, accelerated the subsequent reaction of the wool with propiolactone. At best, about 72 hrs. of treatment at 21°C were required to obtain the desired level of 60% to 70% uptake. Raising the temperature increased the uptake, but reduced the felting, attributable to increased polymerization on the fiber surface rather than in the fiber.

More recently, Fearnley and Speakman [2] studied the reaction of propiolactone with wool. They showed that dry wool did not react with propiolactone in dry ether or in dry benzene, but that reaction did occur when ethyl alcohol was used as solvent. These observations raised the question as to the influence of water and alcohols on the course of this reaction. A study of this question is included in the present investigation. Fearnley and Speakman [2] reported that their propiolactone-treated wool had impaired felting properties, in contrast with the enhanced felting properties reported by Jones and

* Presented at the 123rd National Meeting of the American Chemical Society, Los Angeles, Calif., Mar. 1953.

† Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

Lundgren [4]. This difference may be due in part to the fact that the highest uptake reported by Fearnley and Speakman was only 29.6% propiolactone, and was achieved by conducting the reaction at a temperature of 50°C. Thus, not only was the amount of propiolactone reaction obtained by Fearnley and Speakman insufficient to obtain maximum enhancement of felting properties, but, of even greater importance, since their reaction was conducted at an elevated temperature, it is probable that more of the polymerization occurred on the surface of, rather than within, the fiber. Surface modification covers the scales of the wool fibers and impairs the felting quality. Jones and Lundgren cited microscopic evidence that the propiolactone penetrates the fiber, with deposition of polymer between the spindle cells as a first step.

In any event, the enhanced felting properties and the increased strength of the resulting felts made from propiolactone-treated wool have been confirmed in commercial-scale tests made by two felt manufacturers.

The failure of dry wool to react with propiolactone in dry carbon tetrachloride, ether, or benzene, as reported by Fearnley and Speakman, is confirmed in this work. With water in either the solvent or in the wool, propiolactone reacts readily, although the amount of water required to effect reaction at reasonable rates varies with the solvent employed.

Experimental

Preparation of Wool, Solvents, and Propiolactone

The wool used in this work was obtained from Columbia sheep. It was scoured in the laboratory with carbon tetrachloride, followed by washing with water at about 50°C, and air-dried at room temperature. It was stored until use at 21°C and 65% R.H. Immediately before use, approximately 1-g. samples were dried 3 hrs. at 105°C. Commercial anhydrous ether and benzene were dried by distilling over sodium. Carbon tetrachloride was dried with calcium chloride, followed by distillation, with rejection of the first 5% of the distillate. Commercial absolute methyl and ethyl alcohols were dried with magnesium methoxide or ethoxide according to Fieser's description [3] of the Lund and Bjerrum process. When tested by the Robertson procedure [6], the ethanol so obtained assayed 99.95% ethanol. Laboratory reagent *n*-amyl alcohol was distilled before use; the fraction boiling at 135°–138°C was collected. Technical lauryl alcohol was distilled in vacuum, with collection of the fraction boiling at 134°–139°C at 7 mm. pressure. The oleyl alcohol was N.F. grade and was distilled before use. The propiolactone was supplied by the B. F. Goodrich Chemical Co., and was distilled in vacuum before use, even though all samples were found to have a very short boiling range.

Addition of Propiolactone in Dry Solvents to Dry Wool

Approximately 1 g. of wool was placed in a weighing bottle, dried, accurately weighed, and transferred to a glass-stoppered bottle of 100-ml. capacity. To this was added 10.0 ml. of propiolactone in 40 ml. of benzene. After standing for 90 hrs. at 25.0°C, the contents of the bottle were poured into a Büchner funnel and pressed with the head of a glass stopper until liquid no longer dropped from the funnel. The wool was then returned to the bottle, washed with 25 ml. of benzene, and filtered again. This was followed by six similar water washings. The wool was then returned to the weighing bottle, dried, and weighed. A weight loss of 0.4% was observed. A similar experiment with ether showed a loss of 0.1%. In carbon tetrachloride the wool showed a loss of 0.7% in 50 hrs., but gained 4.0% of its weight in 238 hrs.

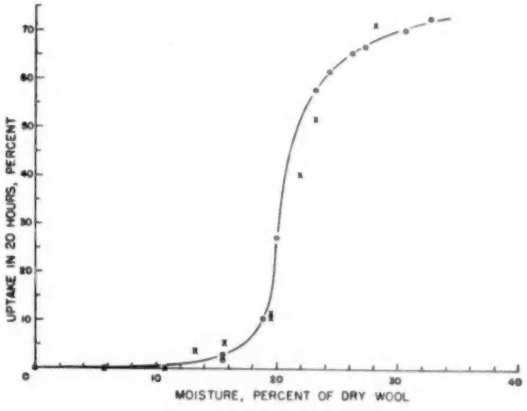

FIG. 1. *Effect of moisture on the reaction of propiolactone with wool. Crosses—water in reagent. Circles —water in wool.*

Effect of Addition of Water

Water, in varying amounts, was added to the propiolactone. The carbon tetrachloride was then added, and the mixture was held for 3 hrs. at 25°C before addition to the wool. The wool-propiolactone reagent was then held for 20 hrs. at 25°C. Addition of water in amounts of less than 10% of the weight of the wool failed to promote the reaction of the propiolactone with the wool. Increasing amounts of water, in the range of 10% to 28%, greatly increased the reaction of the propiolactone with the wool; further addition of water, up to about 220%, had but little effect, and still more water decreased the rate of reaction of propiolactone with the wool. These results are shown graphically in Figure 1 (crosses). It is noteworthy that addition of more than 20% of water resulted in two liquid phases when the carbon tetrachloride was added, but only one phase persisted after the mixture was added to the wool.

Similar results were obtained when wool was allowed to absorb water vapor in varying amounts, and then allowed to react, at 25°C for 20 hrs., with propiolactone in carbon tetrachloride. These data are also represented in Figure 1 (circles). This experiment shows that the same result is obtained when the water is initially present in the wool as when it is added to the propiolactone-carbon tetrachloride reagent.

When propiolactone reacts with wool containing 12.8% water, the initial rate of reaction is very slow, but increases gradually, and then more rapidly after about 80 hrs., when the propiolactone reacted amounts to about 14% of the wool. This is reported in Figure 2 (crosses). This is in marked contrast with the much more rapid and uniform rate of reaction observed when the wool contains 25% water (Figure 2, circles).

We have also measured the rate of the reaction of propiolactone with wool, where the water was present in the wool before addition of the propiolactone-carbontetrachloride reagent, and where the water necessary for the reaction to proceed was added to the propiolactone 3 hrs. before addition of the propiolactone-carbon tetrachloride reagent to the wool. The data, reported in Figure 3, show that the reaction proceeds slightly faster when the water is present in the wool (circles), rather than added to the reagent (crosses). The amount of water present in the wool varied from 32% to 33% of the weight of the dry wool; that added to the reagent was equivalent to 34% to 35% of the dry wool. Since the rate of reaction is not sensitive to the amount of water present, in this range of water content, the difference in rate of reaction cannot be attributed to the difference in water content.

In order to obtain further insight into the role of water in the reaction of propiolactone with wool, the following experiment was carried out. Two wool samples were soaked in water for 2 hrs., filtered, centrifuged, and dehydrated by solvent exchange—*i.e.*, six successive soakings in alcohol, ethyl ether, and carbon tetrachloride, without permitting the fibers to dry. About one-half of the carbon tetrachloride in one of these samples was then distilled *in vacuo* in order to remove any residual water not removed in the solvent treatments. Propiolactone was

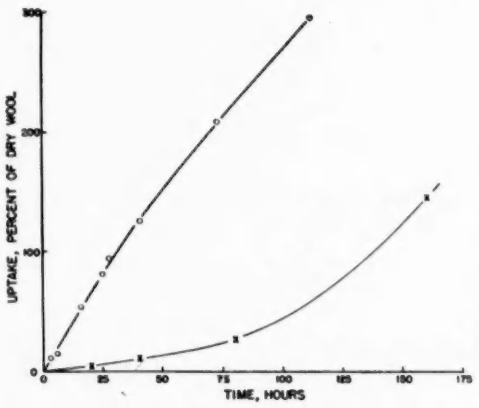

FIG. 2. *Rate of reaction of propiolactone with wool. Crosses—12.5% water in wool. Circles—dry wool, water added to propiolactone reagent equivalent to 25% water in wool.*

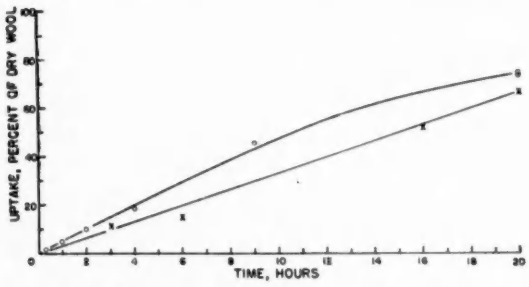

FIG. 3. *Rate of reaction of propiolactone with wool. Crosses—water in propiolactone reagent equivalent to 35% of the dry weight of wool. Circles—water in wool equal to 33% of the dry weight of wool.*

then added, and the rate of reaction of the wool with the propiolactone was determined as described above. In the sample from which part of the carbon tetrachloride was distilled the propiolactone uptake amounted to 17.4%, and in the other sample 15.5%. Hence, the propiolactone uptake of the swollen, anhydrous fibers was about one-fourth that obtained in the presence of water. It would appear that swelling of the fiber is not a prerequisite; however, it should be noted that we have no evidence that the swollen fibers did not collapse during the solvent-exchange treatments. On the other hand, it is possible that water can assist in the reaction, as a catalyst.

Influence of Mechanical and Chemical Treatment of the Wool Fiber on the Reaction of Propiolactone with Wool

Samples of wool were carded for a prolonged period of time in order to effect mechanical damage and to raise the scales. The rate of reaction of propiolactone with this damaged wool, dried or with 12.7% moisture, was not different than with untreated wool.

Wool was soaked in 7% potassium hydroxide in 95% ethanol, and then in 7% sulfuric acid in 95% ethanol, and was washed exhaustively with distilled water, as described by Lindberg [5], to damage the surface of the wool fibers. These wool fibers were then dried and placed in a solution of propiolactone in carbon tetrachloride for 20 hrs. at 25°C. No reaction occurred with wool receiving alkali treatments for periods of 1.5 or 5 min.

Wool samples were soaked for 30 min. in phthalate buffer, pH 4.6; other samples were soaked in phosphate buffer, pH 7.2. The samples were then steamed for 15 min., washed with distilled water, centrifuged to a residual moisture content of 35%, and allowed to react with propiolactone in carbon tetrachloride. Propiolactone uptakes were: pH 4.6 buffer, 64.2%, 65.0%; pH 7.2 buffer, 49.4%, 49.8%.

Effect of Fiber Diameter on Rate of Reaction with Propiolactone

Wool specimens were available from five pure breeds of sheep from a flock owned by Howard Vaughn of Dixon, Calif. These sheep had been pastured together, so that any differences in the wool were assumed to be characteristic of the breed of sheep. The wools had the following average fiber diameters: Rambouillet, 19.9 μ; Columbia, 27.9 μ; Suffolk, 35.0 μ; Navajo, 36.7 μ; and Lincoln, 38.6 μ. A very fine New Zealand wool, designated Tasmanian 120's, having an average fiber diameter of 11 μ, was also available. In the reaction of these wools with propiolactone in carbon tetrachloride, the water necessary for the reaction to occur was added by soaking the wool in water for 10 min., followed by centrifuging for 3 min. at 2,300 r.p.m. Under these conditions the water retained by the wool was equivalent to 46%–47% of the weight of the wool. The results so obtained are reported in Figure 4. They suggest that the rate of reaction of propiolactone with wool increases with the diameter of the fiber, although the differences in rate of reaction are small compared to the differences in fiber diameter. The results obtained from the Suffolk wool are not in agreement with this conclusion. However, the mechanical properties of these fibers have been studied extensively in our laboratory, and in these properties also the Suffolk fibers fail to conform to the pattern established by the other four Vaughn wools.

Substances Other than Water as Promoters of the Reaction of Wool with Propiolactone in Carbon Tetrachloride

We sought other substances that would affect the reaction of propiolactone with wool. These substances included glacial acetic acid, 85% lactic acid,

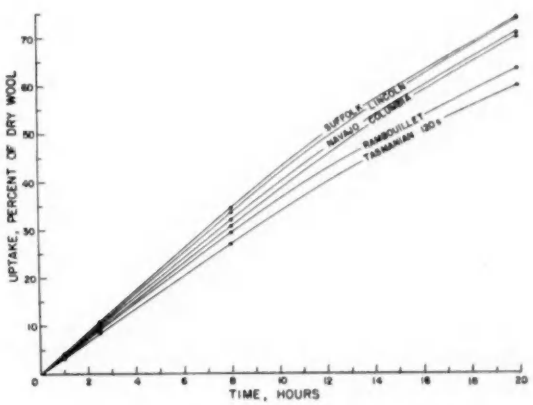

FIG. 4. *Relationship of diameter of fiber to rate of reaction of propiolactone with wool. Average fiber diameters: Tasmanian 120's, 11 μ; Rambouillet, 19.9 μ; Columbia, 27.9 μ; Suffolk, 35.0 μ; Navajo, 36.7 μ; Lincoln, 38.6 μ.*

methanol, ethanol, absolute lactic acid, ethylene chlorohydrin, 1,3-dichloro-2-propanol, phenol, *p*-nitrophenol, dimethyl formamide, trichloroacetic acid, and *beta*-hydroxypropionic acid. The first three substances were the only ones that promoted the reaction of wool with propiolactone in carbon tetrachloride. Addition of 0.5 ml. of glacial acetic acid to the propiolactone-carbon tetrachloride solution before addition of this reagent to the dry wool resulted in a loss of 0.6% in weight. When 5.0 ml. glacial acetic acid was added, a weight increase of 4.8% was found after 20-hrs. reaction period. The water present in the acetic acid (25 mg.) was only about one-sixth that required for the observed propiolactone uptake; hence, the acetic acid must have some slight effect in promoting the reaction. Addition of 2.0 ml. of 85% lactic acid to the propiolactone-carbon tetrachloride reagent resulted in a propiolactone uptake of 7.2%. If the 15% impurity is assumed to be water, sufficient water was added to anticipate an uptake of 71.5% propiolactone. It would thus appear that the lactic acid inhibits the activity of the water in promoting the reaction. The uptake observed in this instance was doubtless due to the water present, since the addition of 2.0 ml. of absolute lactic acid (obtained by distillation of the 85% acid boiling at 68°–73°C at 0.002 mm. pressure) resulted in a weight loss of 0.6%. Addition of 2.50 g. of anhydrous methanol to the propiolactone-carbon tetrachloride reagent resulted in an uptake of 15.6% in 20 hrs.

Addition of 0.30 or 5.00 g. anhydrous ethanol to the propiolactone-carbon tetrachloride reagent resulted in weight losses of 0.4% and 0.1%, respectively. With 20 ml. ethanol and 20 ml. carbon tetrachloride as solvent for propiolactone, the gain in weight was 4.7 mg., or 0.4%. The *beta*-hydroxypropionic acid was prepared by hydrolysis of the lactone (72.0 g., 1 mol) with 18 g. of water at room temperature. After 70 hrs., titration showed the lactone to be 48% hydrolyzed. A portion of this mixture of lactone, water, and acid was distilled, collecting the product boiling at 97°–102°C at 0.002 mm. pressure. Titration showed the distilled product to be 96% *beta*-hydroxypropionic acid; the remaining 4% is probably a polymer of this, since an appreciable amount of a higher-boiling polymer was formed during the distillation. Addition of 2.0 g. of this distilled acid to the propiolactone-carbon tetrachloride reagent resulted in a weight gain of 11.3 mg., equivalent to 1.2% of the dry wool. This small uptake is considered significant, and it thus appears probable that the *beta*-hydroxypropionic acid has a slight activating effect on the reaction of propiolactone with wool.

Propiolactone Uptake in Alcohol-Water Systems

It is of interest to note the results obtained when alcohols replace carbon tetrachloride as the solvent, as reported by Fearnley and Speakman for ethanol. With ethanol as solvent, the rate of propiolactone uptake is increased by addition of water, as when carbon tetrachloride is used as solvent, except that much larger quantities of water are required to attain the maximum rate of uptake. These data are reported in Figure 5A, in which the previously reported data for carbon tetrachloride are recalculated to express the water present as a percentage of the solvent, and reproduced for comparison. Figure 5 (A and B) also present data obtained using methyl, *n*-amyl, oleyl, and technical dodecyl alcohols as sub-

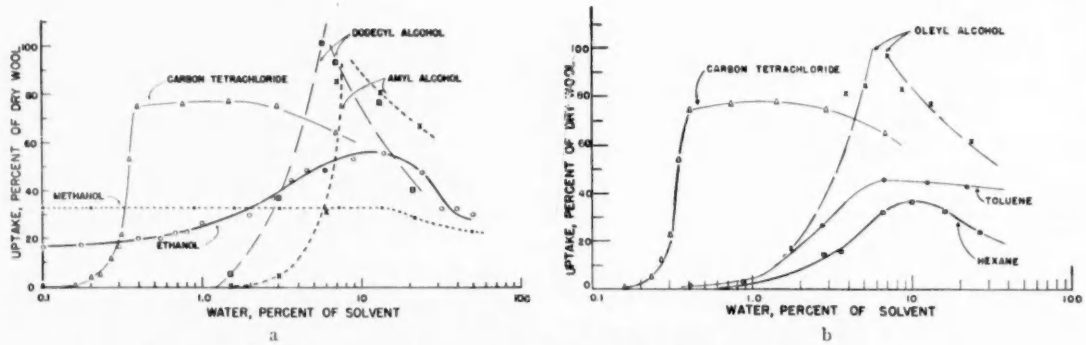

FIG. 5. *Effect of water on the reaction of propiolactone with wool in various solvents.*

stitutes for carbon tetrachloride. The results with methyl alcohol are unusual, in that addition of water is without effect until the water used amounts to 14% of the methanol, or more than five times the amount of wool used. Addition of larger quantities of water resulted in a decrease in the propiolactone uptake. With amyl and lauryl alcohols, as with carbon tetrachloride, no reaction occurred between the propiolactone and dry wool. Here, also, addition of water was effective in promoting this reaction. The sharp peaks obtained on addition of these alcohols to water are accentuated in Figure 4, since a semilogarithmic scale is employed to separate the curves somewhat.

Although propiolactone in dry lauryl alcohol does not react with wool, addition of methyl alcohol to the lauryl alcohol promotes this reaction. Thus, propiolactone uptakes of 12.5%, 55.3%, and 61.4% were obtained in a 20-hr. reaction period when the percentage of methanol in the solvent was 7.0%, 13.1%, and 49.0%, respectively. These values greatly exceed the 33% uptake in methyl alcohol and the total absence of reaction in lauryl alcohol.

Propiolactone is not soluble in oleyl or dodecyl alcohols; hence, these reaction mixtures consisted of two liquid phases in addition to the solid (wool) phase. It was therefore of interest to compare the rate of this reaction in the presence of an immiscible substance of a different type, such as hexane. These results are reported in Figure 5B. Although toluene is a solvent for propiolactone, the results with this solvent (Figure 5B) are not greatly different from those obtained in the presence of hexane. It may also be noted that in the presence of hexane, a more rapid uptake is observed when the moisture is present in the wool, rather than in the propiolactone-hexane mixture. Thus, with water in the wool equivalent to 1.5% of the weight of the hexane (or 41% of the dry wool) the propiolactone uptake was 50.0%, as compared with a 7.5% uptake with the same amount of water added to the propiolactone-hexane reaction mixture.

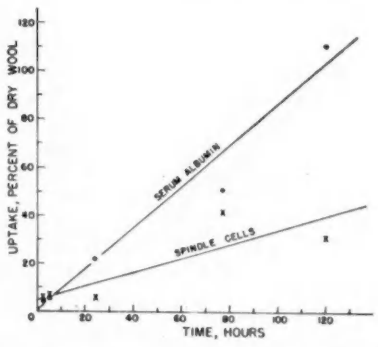

FIG. 6. *Reaction of propiolactone with dry spindle cells and with dry serum albumin.*

Reaction of Spindle Cells of Wool with Propiolactone

Morphologically, the wool fiber consists of elongated particles, known as "spindle cells," encased in an outer tubular sheath. The spindle cells can be isolated by destruction of the outer sheath with cold 6*N* hydrochloric acid [1].

Dry spindle cells prepared in this manner were found to react with propiolactone in dry carbon tetrachloride, in contrast with the results obtained with intact dry wool fibers. The rate of reaction of dry spindle cells with propiolactone in dry carbon tetrachloride and, for comparison, the rate of reaction of dry serum albumin with this reagent are reported in Figure 6. Although the rate of the reaction of propiolactone with spindle cells is only about one-seventh of that observed when moist wool reacts with this reagent, it is considered to be significant that dry spindle cells do react, whereas dry, intact wool fibers do not react.

Discussion

The experiments have demonstrated the striking influence of small amounts of water in promoting the reaction of propiolactone with wool. Excess water in the reaction mixture reduces the amount of reaction with propiolactone, due, presumably, to hydrolysis of the lactone. At least two explanations may be offered for the accelerating influence of small quantities of water. One is that the lactone or a portion of it is hydrolyzed by the water, producing some *beta*-hydroxypropionic acid, which is necessary to initiate the reaction of the lactone with the wool. This possibility is supported by a consideration of the rate of reaction of propiolactone with wool containing 12.5% moisture (see Figure 2). The low initial rate may be attributed to the small amount of *beta*-hydroxypropionic acid produced by reaction of part of the moisture in the wool with the lactone. The amount of free acid would gradually increase as hydrolysis of the lactone proceeded. This mechanism, however, is not supported by the

experiment in which *beta*-hydroxypropionic acid was added to the dry wool and propiolactone, since the acid fails to promote the reaction to any appreciable extent under these conditions. Also of significance is the fact that spindle cells, isolated from wool, react with propiolactone in the absence of water. Evidently, *beta*-hydroxypropionic acid is not necessary for the reaction of propiolactone with wool.

A more consistent explanation for the effect of water is that it swells the wool structure to permit entrance of the propiolactone to reactive sites in the protein molecules within the fiber. The view that preliminary swelling of wool is required for penetration by agents has been advanced on several occasions by Speakman and others, and the data presented in this paper support this view. Similar rates of propiolactone uptake were observed, whether the water was initially present in the wool or was in the propiolactone reagent before addition to the wool. Moreover, the results with the various alcohols as solvents support the theory that preliminary fiber opening is essential to penetration by propiolactone, since methyl and ethyl alcohols are small molecules capable of penetrating and opening the fiber structure. Speakman has shown in his earlier studies that only the lower aliphatic alcohols can penetrate wool [7]. The larger amyl and dodecyl alcohols cannot do this, and hence no reaction occurs in these dry alcohols. Of the greatest significance is the fact that in mixtures of water and amyl, oleyl, or dodecyl alcohols the maximum rate of uptake is 30% greater than the maximum in moist carbon tetrachloride. Evidently the water provides an opening wedge in the wool structure which then permits further structural opening by the higher alcohols, presumably through van der Waals' interactions with appropriate sites on the wool protein network. This interpretation is supported by measurements of the stress-strain behavior of wool fibers in amyl and dodecyl alcohol-water systems. In the dry alcohols, the mechanical properties correspond to those of the dry fibers, indicating no penetration or swelling of the fibers by the dry alcohols. When water is present in the alcohols at concentrations corresponding to that producing a maximum rate of propiolactone uptake, the stress-strain behavior indicates swelling of the fiber to a degree greater than that which occurs in water alone.

This view is probably an oversimplification of the mechanism involved, since it is difficult to account for the fact that the addition of water to methanol fails to increase the rate of reaction, despite the fact that the rate in methanol is only about one-half that in moist carbon tetrachloride. Moreover, it is not unlikely that both water and reactive sites in wool act as catalysts for the polymerization of propiolactone. In this regard, it is significant that no polymerization occurs in the solvent in the absence of the wool.

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(Manuscript received June 16, 1953.)

Letters to the Editor

Short communications in the form of Letters to the Editor are intended to provide prompt publication of significant new research results and to permit an exchange of views on papers previously published in the JOURNAL. These communications are not submitted to formal review as are research papers, and the editors do not assume any share of the author's responsibility for the information given or the opinions expressed. When work previously published in the JOURNAL is the subject of critical comment, the authors of the original paper are given an opportunity to submit a reply, which will be published concurrently when possible.

Influence of Fiber Length on the Milling Shrinkage of Wool Cloths

EAST SYDNEY TECHNICAL COLLEGE
School of Textiles
New South Wales, Australia
July 14, 1953

To the Editor
TEXTILE RESEARCH JOURNAL

Dear Sir:

The results of the following experiments I carried out on woven fabric at the University of Leeds in 1929 might be some contribution to the problem raised in the article "The Felting in Laundering of Wool Blends," by Bogaty, Sookne, Weiner, and Harris (TEXTILE RESEARCH JOURNAL **23**, 114–18 (Feb. 1953)).

Briefly, the influence of fiber length on the milling shrinkage of wool cloth was under consideration, the material used being the following British pedigree wools (described in *Journal of Textile Science*, Leeds University, Aug. 1925) with the following average fiber lengths: Devon Longwool, 9 in.; South Devon, 11 in.; Leicester, 12 in.

Half of each lot of wool was made into woolen cloth and half into worsted, and the fabrics were milled under carefully controlled conditions.

Plots of percentage reduction in area against time were studied, and these were found to agree in the main with the comment on Table IV of the paper by Bogaty *et al.* cited above.

In Figure 1 the influence of fiber arrangement—*i.e.*, woolen or worsted—is revealed, and this was confirmed later by other research carried out at Leeds. Briefly, whilst the longer staples shrank more than the shorter and the worsted more than the woolen, the surface appearance and *evenness* of the milled fabric was not so satisfactory as when short-staple woolen yarns were milled.

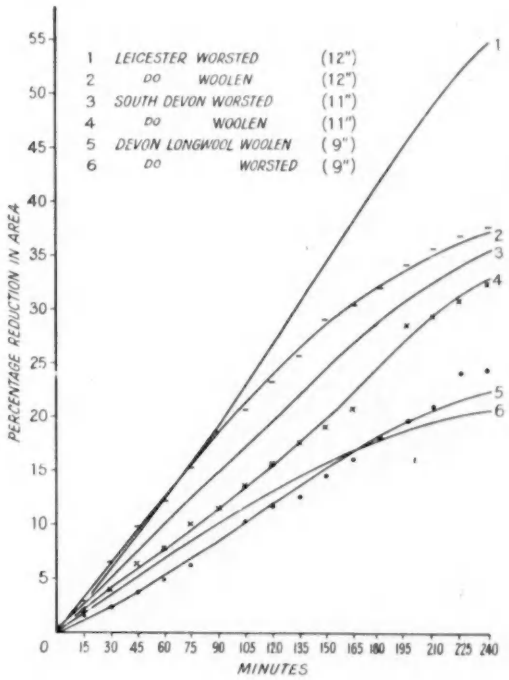
1 LEICESTER WORSTED (12")
2 DO WOOLEN (12")
3 SOUTH DEVON WORSTED (11")
4 DO WOOLEN (11")
5 DEVON LONGWOOL WOOLEN (9")
6 DO WORSTED (9")
PERCENTAGE REDUCTION IN AREA
MINUTES
0 15 30 45 60 75 90 105 120 135 150 165 180 195 210 225 240
5 10 15 20 25 30 35 40 45 50 55

FIG. 1

A. JOHNSON

Heterogeneity of Keratin Fibers

TECHNICAL COLLEGE
Chemistry & Dyeing Dept.
Bradford, England
July 22, 1953

To the Editor
TEXTILE RESEARCH JOURNAL

Dear Sir:

In a recent article, "The Heterogeneity of the Keratin Fibers," Mercer [3] identified membranes in the cortex of the fibers. These membranes were revealed on optical micrographs of transverse sections of oxidized fibers after extraction with mild alkali.

We have performed very similar experiments to those described by Mercer, and have obtained conclusive evidence that these membranes do exist. Transverse and longitudinal sections of peracetic acid-treated fibers [1] were cut, and the sections were treated with $N/10$ ammonium hydroxide solution for 24 hrs. The resistant parts of the cortex were identified as the boundaries of the cortical cells, remnants of cell nuclei, and some fibrils. The peripheral zone of the cortex was not more resistant than the rest of the cortex, and we therefore agree with Mercer that the peracetic acid-ammonium hydroxide treatment of wool and hair does not isolate the "sub-cuticle membrane," as described by Alexander [1].

We have found it more convenient to extract the oxidized protein with sodium hydroxide solution instead of ammonium hydroxide. Figure 1 is a photomicrograph of a transverse section, stained with methylene blue, of peracetic acid-treated wool, after 10 min. in $2N$ sodium hydroxide. We have also examined treated sections in the electron microscope, and found that the resistant boundaries of the cortical cells are very thin membranes. Figure 2 is an electron micrograph of a transverse section of peracetic acid-treated wool, after 5-min. treatment with concentrated sodium hydroxide solution. Here the membranes have fallen on their sides and a few fibrils adhere to them. Electron micrographs of shadowed specimens show that they are of the same order of thickness as the epicuticle [2, 4]—*i.e.*, about 100 Å. We have observed similar membranes on electron micrographs of treated sections of cow-tail hair and rat hair. The treatment of wool and hair fiber sections with $2N$ sodium hydroxide solution at 60°C also isolates these membranes.

It is not possible to decide from our electron micrographs whether these membranes are single

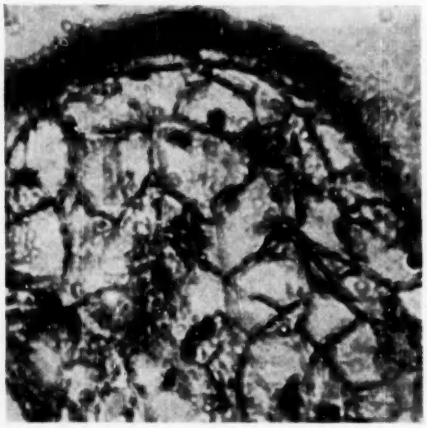

FIG. 1. *Photomicrograph of a transverse section of peracetic acid-treated wool fiber after 10 min. in 2N sodium hydroxide; stained with methylene blue. (Magnification, 1,000 ×.)*

FIG. 2. *Electron micrograph of a transverse section of peracetic acid-treated wool fiber after 5 min. in concentrated sodium hydroxide.*

or double—*i.e.*, whether they are intercellular membranes or "cortical cell membranes." Possibly in the follicle each cell is enclosed in a membrane, and during growth of the fiber, membranes of adjacent cells fuse.

We wish to thank Dr. R. L. Elliott for his interest, the Bradford Dyers' Association, Ltd., for the award of a fellowship to one of us (B.M.), and the Wool Textile Research Council for the award of a scholarship to one of us (M.S.M.).

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B. MANOGUE
M. S. MOSS

The Esterification of Carbohydrates with Formic Acid

THE INSTITUTE OF PAPER CHEMISTRY
Appleton, Wisconsin
September 30, 1953

To The Editor
TEXTILE RESEARCH JOURNAL

Dear Sir:

The esterification of starch and cellulose with formic acid was used by Nickerson [4] as a means of estimating the accessibility of the cellulose. He carried out the esterification with a large excess of formic acid, and determined the degree of esterification in the washed products by a modified Eberstadt [5] saponification technique.

Tarkow and Stamm [6] studied the esterification of carbohydrates with formic acid. They carried out the esterification for 15 hrs. at 55°C, and determined the excess of formic acid by reaction with acetic anhydride to form carbon monoxide, which was measured by volume. They found that only the primary hydroxyls of cellulose were esterified, and that the degree of esterification could be used as a measure of accessibility of the cellulose.

Attempts to apply the Tarkow and Stamm method gave unsatisfactory results. When the ratio of formic acid to carbohydrate was increased over the range used by these authors, the amount of combined formic acid did not level off at the theoretical value given by them. In addition, it was found difficult to obtain uniform wetting when cellulose was used, and results were variable because of poor contact of the reactants.

These difficulties suggested the study of a modified method in which the extent of esterification is determined directly by titration of the water formed during the esterification reaction, using the Karl Fisher reagent. This procedure has been well established through previous studies [3], and is especially applicable to the present problem. Since one mole of water is formed for each mole of hydroxyl esterified, the simple titration for water gives immediately a quantitative measure of the degree of esterification.

Because the measurement is direct, rather than by difference as in the Tarkow and Stamm method, a larger ratio of formic acid to carbohydrate can be used. This permits more even wetting of the material, and allows the study of the reaction at larger ratios of formic acid to carbohydrate.

Experimental

The carbohydrate to be esterified was placed in a 100-ml., round-bottom, glass-stoppered flask, dried for 2 hrs. at 60°C in a vacuum oven, and weighed. The desired amount of formic acid was weighed into the flask, and the reaction was allowed to proceed under the time and temperature conditions chosen. At the end of the reaction period the flask was cooled and 25 ml. of a 1 : 1 pyridine-methanol mixture was added. The flask was again cooled to room temperature, and the water was determined by titration with Karl Fischer reagent. A slight excess of Fischer reagent was added and the solution was back-titrated with methanol-water solution, using a dead-stop electrometric titration apparatus adapted from McKinney and Hall [2]. The amount of water found was corrected by subtracting that introduced with the formic acid and the pyridine-methanol mixture, and the remainder was attributed to the esterification reaction. The formic acid used

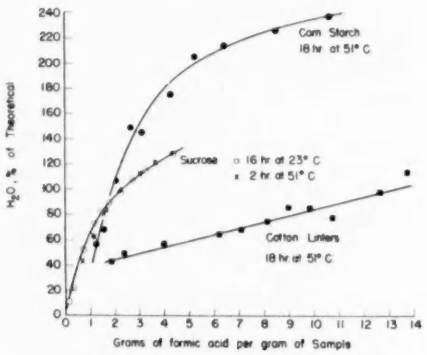
Corn Starch
18 hr. at 51° C.
Sucrose
○ 16 hr. at 23° C.
× 2 hr. at 51° C.
Cotton Linters
18 hr. at 51° C.
H2O, % of Theoretical
Grams of formic acid per gram of Sample

FIG. 1. *Esterification of carbohydrates with formic acid.*

assayed 99.3% by titration with standard alkali and contained 0.7% water by the Karl Fischer titration.

Samples of sucrose (0.5 g.) were esterified with formic acid for 16 hrs. at 23°C, 2 hrs. at 23°C, and 2 hrs. at 51°C. The results obtained at 23°C for 2 hrs. were erratic, and thus it appears that the reaction time is too short at this temperature. The results obtained at 23°C for 16 hrs. and at 51°C for 2 hrs. were nearly identical, and are shown in Figure 1.

According to Tarkow and Stamm, the esterification of sucrose results in the formation of the triformate, for which the theoretical yield of water would be 15.79%. This figure was used as the theoretical value in the calculation for Figure 1. Because of the limitation of the method they used, Tarkow and Stamm could not use a ratio of formic acid to sugar larger than about 1.2:1. In the present work, this limitation did not exist, and the ratio was increased to more than 4:1. The amount of combined formic acid did not level off at the calculated value for the triformate, but continued to increase slowly as more formic acid was added.

The esterification of starch is supposed to result in the formation of the monoformate, with a theoretical yield of water of 11.11%. Samples of cornstarch (No. 144 of Corn Products Refining Co.) weighing 0.2–0.5 g. were esterified for 18 hrs. at 51°C. The curve in Figure 1 shows that the esterification proceeds far beyond the monoformate stage as the ratio of formic acid to starch is increased.

The esterification of purified cotton linters was carried out under the same conditions used for cornstarch, and should give the same results if all the hydroxyl groups are completely accessible. Even with the large ratio of formic acid to linters, adequate physical contact was not always obtained and some results were erratic. However, it is clearly shown that some secondary hydroxyl groups must be esterified if the accessibility is in fact less than 100%.

The possibility that water is formed upon the addition of the pyridine-methanol mixture to the carbohydrate and formic acid was examined for the case of sucrose. An air-dry sample of sucrose was found to contain 0.02% water, and a similar sample added to a flask in which the formic acid had been treated with the pyridine-methanol mixture apparently contained 0.27% water. Although some water may be formed in this way, the amount appears to be small compared to that found under the conditions of time and temperature used for the esterification reaction.

Discussion

The results obtained indicate that more hydroxyls are available and that esterification with formic acid proceeds to a greater extent than was supposed previously. The lower degrees of esterification obtained by Tarkow and Stamm may have resulted from the limitation of approximately 1:1 in the formic acid-carbohydrate ratio which could be used in their method. In the method used by Nickerson, part of the formic acid may have been lost by hydrolysis during washing in preparation of the formate. The general instability and ease of hydrolysis of formate esters have been noted [1]. If, as Tarkow and Stamm suggested, secondary hydroxyls are formylated only with difficulty, then the resulting ester may be very readily hydrolyzed. Although the present work suggests formylation of secondary hydroxyl groups, it is possible that the reaction is much slower than with primary groups. No opportunity for loss of combined formic acid is permitted, because the measurement of esterification is made in the presence of a large excess of formic acid.

If the starch is assumed to be 100% accessible, then from the ratio of the amounts of water formed with cornstarch and cotton linters (for example, at 10 g. of formic acid per gram of sample) one can calculate that the cellulose is about 35% accessible. This yields a value in the range of presently accepted figures for the accessibility of cotton, and it represents a procedure which is comparable to that of

Nickerson and of Tarkow and Stamm. However, in view of the nonspecific character of the formylation reaction found in this work, the procedure would seem of doubtful validity.

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B. L. BROWNING
L. O. SELL

Society of Chemical Industry (British) Symposium

The Chemistry and Physics of Synthetic Fibers

The Plastics and Polymer Group of the Society of Chemical Industry will conduct a symposium called "The Chemistry and Physics of Synthetic Fibers." It will be held in London, March 24–26, 1954. Papers will be presented and discussed on the chemical and physical basis of fiber formation and the properties of fibers in relation to the molecular structure and conditions of formation.

It is planned to have contributions from other countries in addition to those already promised from all the major organizations dealing with synthetic fibers in the United Kingdom. Preprints will be available.

Further details concerning the meeting may be obtained from A. R. Burgess, Society of Chemical Industry, 56 Victoria St., London, S.W. 1.

INDUSTRIAL SECTION

The Effect of Relative Humidity on Micronaire Readings

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Introduction

THE EFFECT of relative humidity on various physical properties of cotton fibers has been recognized for many years. Even though fineness is extremely important with regard to the manufacturing performance of cotton and the quality of the finished product, very little data are available indicating the extent to which Micronaire readings are influenced by relative humidity. The Micronaire operating instructions state that: "All scales have been calibrated under atmospheric conditions of 70°F and 65% relative humidity. Conditions near these points will have little effect when checking cotton." Since it is accepted that relative humidity affects the Micronaire reading, a preliminary investigation has been made to ascertain the magnitude of this effect.

Since temperature has a much smaller influence on moisture regain than does relative humidity [5], it seemed logical that the effect of temperature on Micronaire reading would be less than that of relative humidity; consequently, the temperature effect was not investigated in this study.

Procedure

The humidity cabinet which was designed and constructed for this experiment is shown diagramatically in Figure 1. It is 37 in. × 21 in. × 9 in., with plywood sides and bottom and a Plexiglas top. All cracks were filled with putty, and four coats of varnish were applied inside and outside to prevent the entry of air and moisture. In order to provide for good air circulation, a piece of galvanized ¼-in. mesh screen, on which the samples were placed, was supported ¾ in. from the bottom of the box. A narrow shelf was nailed to the sides and back of the cabinet about 3 in. from the top to provide storage space for the tin weighing cans. The samples were enclosed in these cans before they were removed from the cabinet for Micronaire determinations. Two 4-in. holes were cut into the front section, and a pair of long rubber gloves were sealed

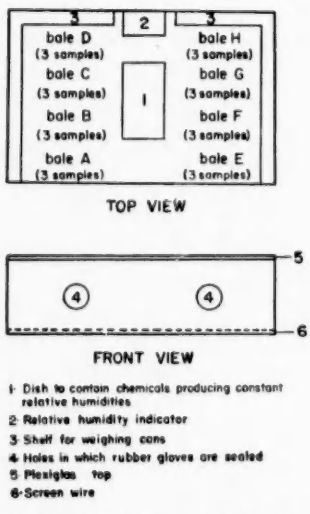

FIG. 1. *Schematic drawing of humidity cabinet.*

FIG. 2. *Photograph of humidity cabinet.*

into these holes. Figure 2 illustrates how all handling of the samples, prior to removal from the cabinet, was accomplished. A Weston 2201 Relative Humidity Indicator, equipped with a battery-driven auxiliary fan, was placed in the center of the cabinet towards the back. This indicator operates on the wet and dry bulb principle, and the manufacturer claims an over-all accuracy of ± 1% relative humidity. The compounds used to produce constant relative humidities were placed in a shallow dish which occupied the center portion of the cabinet.

Eight bales, covering a wide range of fineness, were selected for this study. Seven of these bales were American Upland type cottons, and one, the coarsest, was an Asiatic type. A portion of each bale was carded to remove the trash and blend the cotton. Three samples of the card web from each bale were arranged in the cabinet, a desiccant was placed in the dish, and the Plexiglas top was sealed with putty. The relative humidity was reduced to 20%; and after it remained at this value for 24 hrs., the samples were enclosed in the tin weighing cans, using the rubber gloves as described above. The seal was broken, and the cans containing the 24 samples were removed. The sample weight was rapidly adjusted to 3.240 g. (50 grains), and at no time were the cottons exposed to the room atmosphere for more than a few seconds. The Micronaire determinations were made soon after weighing; and the time interval required to open the weighing can, remove the sample, insert it into the chamber, and read the Micronaire was very short. It was assumed that the change in moisture content because of exposure to the atmosphere in the fiber testing laboratory was negligible.

After each determination, the sample was again enclosed in its weighing can and replaced in the humidity cabinet. The desiccant was removed and a saturated solution of calcium chloride was placed in the dish. After the cabinet was sealed, the cottons were removed from the cans and arranged on the wire screen. The samples were exposed until the relative humidity increased to an equilibrium value and remained at that value for at least 24 hrs.; then the above procedure was repeated. Various saturated solutions were used to produce succes-

TABLE I. MICRONAIRE READINGS (CURVILINEAR SCALE) FOR ABSORPTION PHASE

R.H. (%)		*A*	*B*	*C*	*D*	*E*	*F*	*G*	*H*
20		2.39	3.02	3.52	4.28	4.69	5.01	6.18	7.20
		2.39	2.99	3.55	4.35	4.77	5.05	6.15	7.28
		2.39	2.99	3.47	4.30	4.72	5.00	6.21	7.22
	mean	2.39	3.00	3.51	4.31	4.73	5.02	6.18	7.23
42		2.42	3.09	3.59	4.45	4.81	5.20	6.32	7.40
		2.41	3.09	3.55	4.50	4.83	5.20	6.35	7.35
		2.42	3.09	3.58	4.48	4.82	5.18	6.36	7.40
	mean	2.42	3.09	3.57	4.48	4.82	5.19	6.34	7.38
59		2.43	3.13	3.58	4.52	4.85	5.22	6.45	7.45
		2.42	3.10	3.59	4.49	4.83	5.18	6.40	7.45
		2.44	3.12	3.62	4.50	4.83	5.19	6.42	7.42
	mean	2.43	3.12	3.60	4.50	4.84	5.20	6.42	7.44
65		2.46	3.15	3.65	4.55	4.95	5.25	6.60	7.50
		2.43	3.13	3.62	4.60	4.98	5.25	6.58	7.52
		2.44	3.18	3.65	4.58	4.96	5.27	6.56	7.54
	mean	2.44	3.15	3.64	4.58	4.96	5.26	6.58	7.52
73		2.47	3.16	3.67	4.58	4.98	5.35	6.73	7.54
		2.45	3.17	3.63	4.63	5.00	5.29	6.68	7.58
		2.46	3.19	3.66	4.60	4.98	5.31	6.62	7.60
	mean	2.46	3.17	3.65	4.60	4.99	5.32	6.68	7.57
77		2.47	3.15	3.71	4.65	5.00	5.35	6.75	7.55
		2.42	3.20	3.72	4.66	5.10	5.34	6.71	7.60
		2.48	3.19	3.75	4.64	5.00	5.32	6.65	7.63
	mean	2.46	3.18	3.73	4.65	5.03	5.34	6.70	7.59
91		2.55	3.24	3.79	4.65	5.15	5.50	6.85	7.90
		2.52	3.21	3.80	4.70	5.15	5.51	6.86	7.85
		2.51	3.24	3.80	4.67	5.16	5.45	6.82	7.80
	mean	2.53	3.23	3.80	4.67	5.15	5.49	6.84	7.85

TABLE II. MICRONAIRE READINGS (CURVILINEAR SCALE) FOR DESORPTION PHASE

R.H. (%)		*A*	*B*	*C*	*D*	*E*	*F*	*G*	*H*
82		2.45	3.16	3.60	4.58	4.94	5.30	6.45	7.56
		2.43	3.12	3.64	4.54	4.95	5.28	6.44	7.55
		2.47	3.15	3.70	4.57	4.97	5.27	6.48	7.50
	mean	2.45	3.14	3.65	4.56	4.95	5.28	6.46	7.54
80		2.48	3.13	3.62	4.50	4.82	5.18	6.26	7.18
		2.43	3.11	3.61	4.49	4.85	5.16	6.29	7.21
		2.48	3.18	3.67	4.50	4.83	5.19	6.30	7.15
	mean	2.46	3.14	3.63	4.50	4.83	5.18	6.28	7.18
66		2.44	3.10	3.57	4.43	4.82	5.20	6.30	7.12
		2.43	3.09	3.58	4.45	4.78	5.17	6.29	7.15
		2.42	3.08	3.61	4.46	4.82	5.19	6.28	7.15
	mean	2.43	3.09	3.59	4.45	4.81	5.19	6.29	7.14
57		2.42	3.07	3.54	4.35	4.78	5.05	6.29	7.10
		2.40	3.09	3.50	4.40	4.75	5.07	6.26	7.12
		2.41	3.08	3.56	4.35	4.72	5.02	6.24	7.08
	mean	2.41	3.08	3.53	4.37	4.75	5.05	6.26	7.10
47		2.42	3.02	3.51	4.37	4.75	5.10	6.32	7.03
		2.39	3.05	3.48	4.38	4.79	5.02	6.30	7.10
		2.42	3.06	3.53	4.33	4.70	4.95	6.19	7.11
	mean	2.41	3.04	3.51	4.36	4.75	5.02	6.27	7.08
37		2.42	3.10	3.58	4.42	4.82	5.16	6.38	7.25
		2.40	3.05	3.48	4.58	4.85	5.08	6.35	7.20
		2.42	3.10	3.62	4.58	4.85	5.12	6.35	7.28
	mean	2.41	3.08	3.56	4.53	4.84	5.12	6.36	7.24
19		2.40	3.08	3.48	4.44	4.75	4.97	6.08	6.95
		2.38	3.02	3.44	4.40	4.67	5.05	6.12	7.05
		2.42	3.07	3.52	4.41	4.78	5.09	6.15	7.10
	mean	2.40	3.06	3.48	4.42	4.73	5.04	6.12	7.03

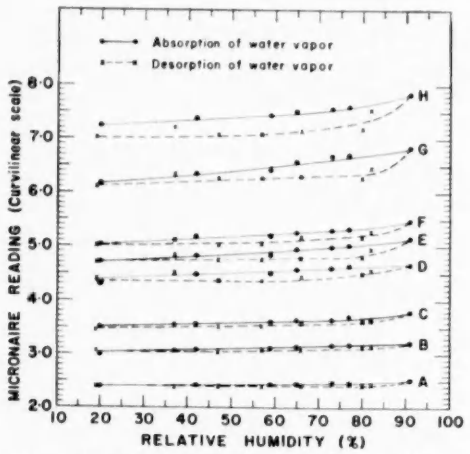

FIG. 3. *The effect of relative humidity on Micronaire reading (temperature, 72.5°F).*

sively higher humidity levels during the absorption phase. In a similar manner, the relative humidity was decreased in order to obtain the desorption data. The relative humidity was much slower in reaching an equilibrium value during the desorption phase; consequently, sulfuric acid, in varying concentrations, was substituted for the saturated solutions and equilibrium was reached in a reasonable length of time. The temperature was maintained at 72.5° ± 1.5°F during the entire experiment.

Results and Discussion

The Micronaire readings obtained during the absorption phase are shown in Table I. A similar set of data for the desorption phase is given in Table II. The mean values from both sets of data are presented graphically in Figure 3, from which the following observations may be made: (*1*) for a given cotton, as the relative humidity increases its Micronaire reading increases; (*2*) for a given relative humidity, the slope of the curve increases as the Micronaire reading increases; (*3*) the difference between the absorption curve and the desorption curve increases as the Micronaire reading increases. The last two factors are probably due to the construction of the curvilinear scale, since the divisions become closer together as the reading increases.

According to Urquhart and Williams [4], in the graph of moisture regain *versus* relative humidity, the desorption curve lies above the absorption curve. Based on this accepted relationship, it would seem that the desorption curves of Figure 3 should lie above the corresponding absorption curves—but this is not the case. A possible explanation of this apparent discrepancy is that the change in Micronaire reading, due to a change in relative humidity, is composed of two separate factors. The weight of "dry" cotton in a 50-grain sample depends upon the moisture regain, and the Micronaire reading would increase as the amount of "dry" cotton decreased. This "weight factor" would then tend to cause the Micronaire reading to increase as the relative humidity increased, and it would also tend to cause the desorption curve to lie above the absorption curve, as mentioned above. The second factor counterbalances the effect of this first factor to some extent. As the relative humidity increases, the fibers in the 50-grain sample will swell due to the absorption of water vapor [1, 2, 3]. This swelling will tend to reduce the Micronaire reading. At a given relative humidity the moisture regain is greater during the desorption phase than during the absorption phase; hence, the fibers would be more swollen during desorption, and the desorption curve representing this "swelling factor" would lie below the absorption curve. The actual, observed change in Micronaire reading, due to a change in relative humidity, may be considered as the resultant of these two opposing factors. Apparently, the weight factor is greater than the swelling factor, since the Micronaire reading does increase with relative humidity; however, the spread between the absorption and desorption curves due to the swelling effect is apparently greater than that due to the weight effect, since the resultant desorption curves of Figure 3 do lie beneath the resultant absorption curves.

The primary interest of this preliminary investigation lies in the numerical data presented in Figure 3, rather than in any conclusions or theories drawn therefrom.

Acknowledgment

This study was planned and conducted under the guidance of Earl E. Berkley, Director of the ACCO Fiber & Spinning Laboratory.

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(Manuscript received July 14, 1953.)

The International Numbering of Yarns and Threads

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THE NUMBERING SYSTEMS which at the present time are used in the various countries and in the various branches of the textile industry for characterizing the size—or the fineness—of yarns and threads are often complex and contradictory, and sometimes outdated. For example, the same yarn, with the same weight per unit length, may be characterized by different figures, depending on the unit system used (Table I).

It is evident from this table that not only are the characterizing numbers very different for the same yarn, depending on the unit system, but also the conversion from one unit system to another results in numbers with decimal figures; moreover, certain unit systems give numbers which vary inversely with the size of the yarn, while others give numbers which vary directly with the size of the yarn.

The situation is still more complex and undesirable in that the unit system used not only varies from one textile to the other (as indicated in Table I), but it also varies for the same textile fiber, depending on its stage in processing and on its final end-use.

Thus, it is common practice to use the following unit systems:

For rayon staple in different stages of processing or on its final end use: in the fibers as produced, denier (direct, metric, but not a decimal unit)

For rayon staple in tow and sliver,† the weight in grams per meter (direct, metric, and decimal)

For rayon staple in fine spun yarns, British cotton number (inverse and nonmetric unit)

For rayon staple in middle-size yarns, British wool number (inverse and nonmetric unit)

For rayon staple in coarse yarns, British flax number (inverse and nonmetric unit)

For rayon staple in fabrics, the weight in grams per meter (direct metric and decimal) or in grams per square meter (direct, metric, and decimal)

In consideration of these anomalies, which result in great and undesirable complications in international trade and between different branches of the textile industry, the Textile Committee ISO/TC/38 of the International Standardization Organization in its session at Bournemouth, England, June 1951, with fifteen nations‡ represented, decided unanimously to adopt the following resolution (Resolution No. 13):

"Technical Committee ISO/TC/38 Textiles reaffirms the proposal to use, for all textile materials, one direct decimal numbering system, based on metric units, namely, grams for weight and metres for length and their multiples or sub-multiples; the specific units used must be stated in all cases. The combination grams-per-ten-kilometres is designated as a 'grex.' The combination grams-per-kilometre is designated as a 'tex.' It is recommended that member countries encourage the use of this system in their own countries."

This resolution, which marks a date to remember in the history of metrology, has not yet produced noticeable effects. The reasons for this condition vary.

Of course the change—for any one industry—from one measuring system to another entails many adaptation difficulties and the overcoming of many traditions. Nevertheless, these difficulties are not as important in the case of the textile industry as they can be in some other industries, because the adoption of the new units does not require the replacement

TABLE I

Unit system used	Characterizing yarn number	
	Example *I*	Example *II*
Metric number	45	6
Denier	200	1500
British cotton number	26.57	3.54
British wool number	39.86	5.32
British jute, hemp, flax number	74.41	9.92
Grams per 1,000 meters of yarn	22.2	167

* Director of Research.

† *Editor's note:* In America, current practices employ other units in addition to those noted by the author—*e.g.*, in picker lap, the weight in ounces per yard; in card sliver, the weight in grains per yard.

‡ Belgium, Canada, Czechoslovakia, Denmark, France, India, Italy, Netherlands, New Zealand, Norway, South Africa, Sweden, Switzerland, United Kingdom, United States of America.

of manufacturing equipment, as it would in certain other industries.

Such changes were made in France during the German occupation in World War II, the French rayon and synthetic yarns industry was obliged to change its numbering system, going from the denier unit (direct numbering system, on a 9.000 m. base) to the metric number (inverse numbering system, on a 1.000 m. base). After the war the industry returned back to the denier unit. Neither of these two changes provoked serious trouble.

Another example of a change in measuring systems was in Spain, where a decree dated September 15, 1947, published September 16, 1947, in the official *State Journal*, specified that:

"1) On and after December 1st all single and plied yarns will be specified and furnished using the decimal, metric, numbering system, in which the yarn number is the weight in grams of 1,000 meters of yarn.

2) The basic unit of that system is named TEX, and is the number of a yarn of which the weight is 1 gram per 1,000 meters length. The multiples and sub-multiples of that basic unit will be formed by adding the corresponding prefixes of the decimal metric system of weights and lengths.

3) There is established a period during which both systems will co-exist, and during which it must be indicated, for confirmation of the number previously used, the equivalent number in the new system, followed by the word TEX, the new number and the unit name being in parentheses.

4) This co-existence period will be maintained as long as necessary for a definitive adoption of the new system without provoking any difficulty or trouble in the industry."

This wise enactment is now actually used in Spain, as can be seen by the rayon labels reproduced in Figure 1.

One of the chief reasons, and perhaps the chief reason, why the Bournemouth resolution has not, up to now, come into more general use can be found in its lack of precision. The ISO Textile Committee TC/38, divided in its opinion between the two proposals—the tex unit and the grex unit—was led to recommend both of these units, since both conform to the general specification of a direct, decimal, and metric unit. But unfortunately, however close their relationship compared with the present diversity of the old units, the fact has not been sufficiently emphasized that the units grex and tex are derived from the same fundamental basic units (grams and meters) and that, as will be seen below, they differ principally in the use of multiples and submultiples of the grex and tex units. The seeming diversity in these units results in many reservations. As a consequence,

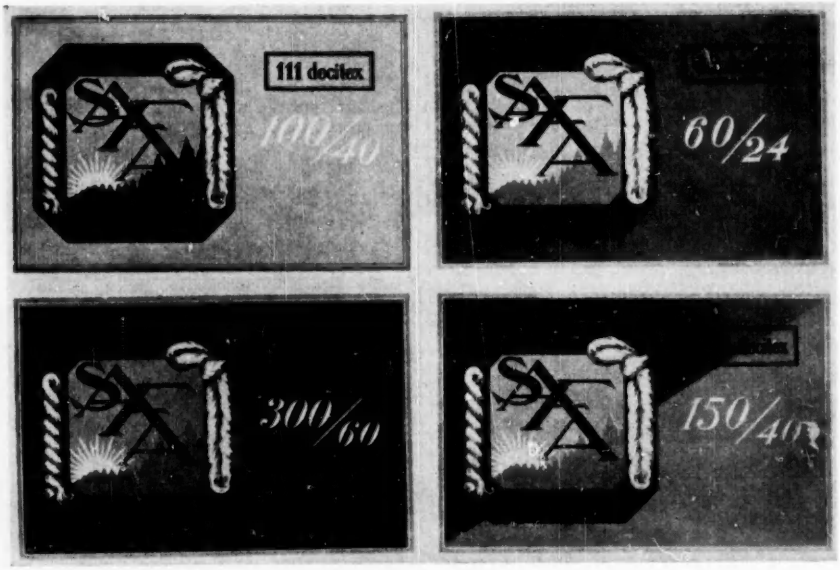


FIG. 1

when considering the adoption of one or the other of these basic units, the user may reasonably ask himself if this is the time to adopt one of them, when there is the possibility that the other one will be much more widely used tomorrow.

Therefore, the Bournemouth resolution did not resolve the problem, and while it has established a very important principle, it has not secured its application. It can even be asked if that resolution does not risk producing the opposite effect to the unification which was desired. Indeed, seeing the struggle between the tex unit and the grex unit, the supporters of the traditional numbering systems feel themselves much more justified in their static position. We believe there is no doubt but that if the ISO Textile Committee TC/38 had been able to agree on only one basic unit, either tex or grex, that basic unit would already be used in international trade, at least in certain important branches of the textile industry.

As the result of a recent inquiry among some international professional organizations, it seems that in Europe a definite majority favors the tex unit. Nevertheless, opinion is always divided. Thus, for instance, in Great Britain The Textile Institute recommends the tex and the British Rayon and Synthetic Fibers Federation prefers the grex. In the U. S. the grex unit seems to be favored, but up to now without much practical use. The tex system, already the only legal unit in Spain, is also partially applied in certain other European countries.

The chief difference between the use of the grex unit and the tex unit seems to be based on the use of multiples and submultiples—more, perhaps, than on the choice of the basic unit. The tex system employs all decimal multiples and submultiples of the basic unit.

Name of unit	Abbreviation	Value
millitex	mtx.	mg./km.
centitex	ctx.	cg./km.
decitex	dtx.	dg./km.
tex	tx.	g./km.
Decatex	Dtx.	Dg./km.
hectotex	htx.	hg./km.
kilotex	ktx.	kg./km. $(= \text{tx.} \times 10^3)$

Among these multiples and submultiples, those which seem to be the most useful for the various branches of the textile industry, and chiefly for rayon and synthetic fibers, are the following: centitex, for staple fibers; decitex, for continuous filament yarns; decatex (or perhaps hectotex), for cabled yarns (plied yarns); and kilotex, for slivers and/or tows (which already are generally numbered in grams/meter, which is an equivalent unit).

The grex system emphasizes only three units.

Name of unit	Abbreviation	Value
grex	gx.	g./10 km.
kilogrex	kgx.	kg./10 km. $(= \text{gx.} \times 10^3)$
megagrex	Mgx.	1,000 kg./10 km. $(= \text{gx.} \times 10^6)$

In a relatively recent paper, Hentschel (*Textil-Praxis* **9**, 660 (1951)) suggested replacing the plurisyllabic word "kilogrex" by a new monosyllabic word, "mex."

This suggestion presents an interesting idea, to which we will return later, but first we wish to point out that the choice of that word for a unit of these dimensions is founded on a basic error. Hentschel writes:

"That designation (Kilogrex) which scientifically cannot be assailed, as distinct from the terms Grex and Tex, has the defect that it is not monosyllabic; for that reason, I urge the adoption of the word *'Mex' derived by abbreviation of 'Megatex'*, and represented by the symbol 'mx.'"

In international metrology the prefix "mega" connotes 10^6. Then, the grex (*i.e.*, g./10 km.) being equivalent to the decitex (dg./km.), it is obvious that the kilogrex is the equivalent of hectotex—that is, to 10^{-4} megatex only.

Taking account of the above reservations, the idea of having monosyllabic words for the most important terms in the numbering unit scale has great appeal. In addition to the terminological simplification it would produce, it would also permit the harmonious combination of the two proposed systems in a single one. In such a system, the word "mex" proposed by Hentschel could be used to advantage, provided its place in the scale was based on its proper etymology. Such a relation is easy to find if we recall the existence of the prefix "myria," which connotes 10^4. It is then possible to admit the word "mex" as an abbreviation of "myriagrex" to designate the unit 1 gram/meter—that is, 10^4 grex, the size which is generally and constantly used for slivers and/or tows. Such a general and constant use seems sufficient to justify, and even to require, a specific and short name.

Equally important in the scale is the size 0.01 mg./m., the most general use of which is in the numbering of staple fibers. This size corresponds to 1 centitex or 0.1 grex. It could be designated by "dex," derived from the abbreviation of "decigrex."

On the contrary, it does not seem necessary to

TABLE II

Size in g./m.	Expression in tex (grex) units	Expression in tex (grex) units	Monosyllabic system Name	Monosyllabic system Symbol	Examples of use
0.000 01	centitex	0.1 grex	dex	dx.	noncontinuous fibers (staple, cotton, etc.) individually numbered
0.000 1	decitex	grex	grex	gx.	fine yarns (silk, rayon, synthetic yarns, etc.)
0.001	tex	10 grex	tex	tx.	medium and coarse yarns, plied yarns, etc.
1	kilotex	10 kilogrex (=1 myriagrex)	mex	mx.	slivers, tows, cords, etc.

have specific names for the intermediate sizes between 1 mg./m. (that is, 1 tex) and 1 g./m. (that is, 1 mex, following the above suggestion). These intermediate sizes can be expressed in tex without any trouble, using numbers of from one to three figures.

The application of the principles discussed above would lead to a system using the monosyllabic terms listed in Table II.

In case it is considered necessary to choose a special word for the intermediate size 0.1 g./m., corresponding either to 100 tex or 1,000 grex, we suggest the word "plex," derived by abbreviation of polygrex, "px."

It would not be the first time in the history of metrology that units which are decimal multiples or submultiples of each other were, for convenience, designated by different words—for example, in length units, the simultaneous existence of meter, micron, Ångström; in area units, the square meter and the acre; in weight units, the gram and the ton, etc.

The combination of the two units tex and grex which the suggested monosyllabic system would in a similar way realize would probably make the general use of these units easier, since such a combined system could be put to use in all countries and in all branches of the textile industry by a similar decision, whatever the preferred basic unit might be. It would indeed be sufficient that such decision only specify the words chosen for each chief multiple or submultiple, and then, whatever the basic unit might be, the same language would be spoken in each textile branch and in every country.

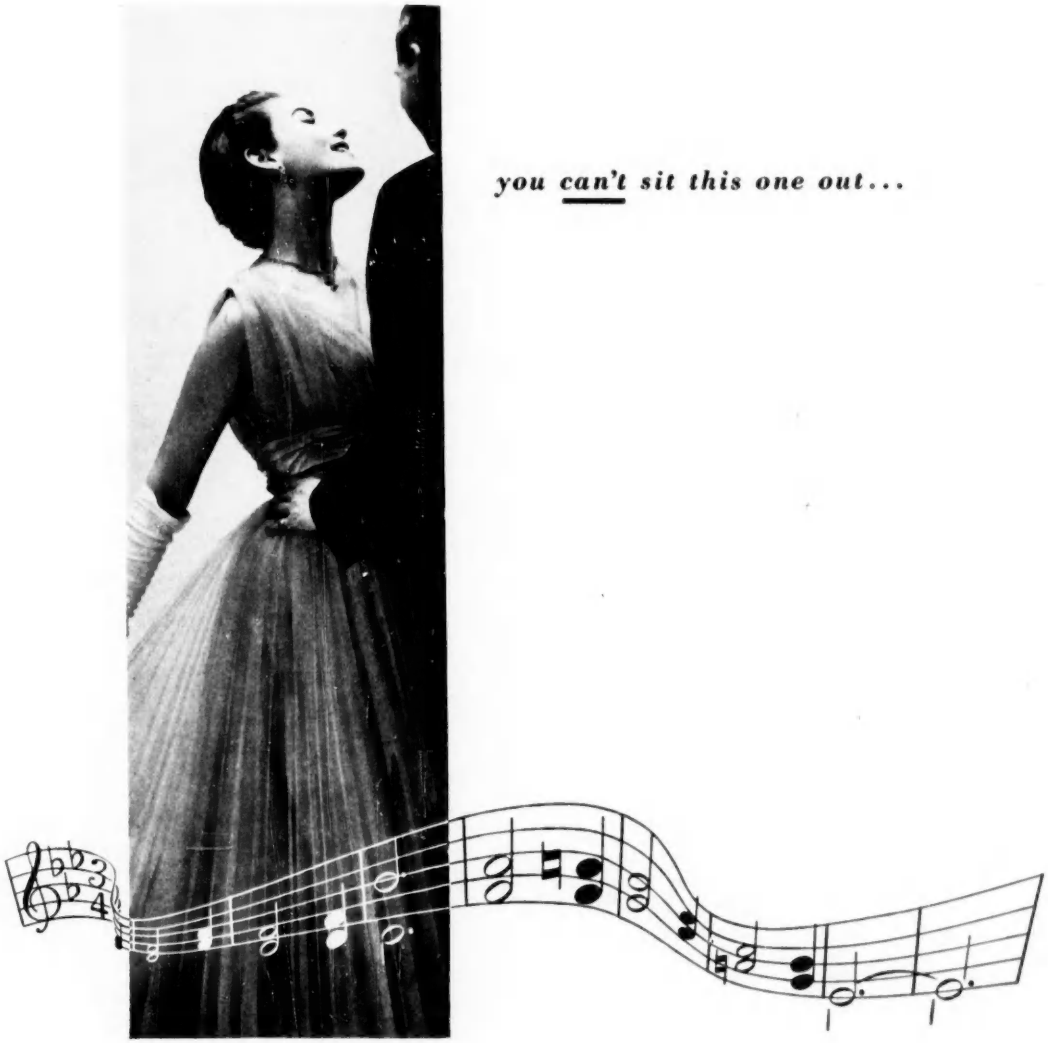
It seems both useful and desirable that the application of the direct, decimal, and metric numbering system unanimously recommended by the Textile Committee of the International Standardization Organization (ISO) be achieved rapidly. At a time when new textile fibers, and consequently fiber mixtures, are being developed rapidly, at a time of interpenetration of different branches of the textile industry, at a time when international trade tends to reach its highest development, and at a time when standardization takes on greater and greater importance, it seems extremely unwise to perpetuate the complex and incoherent state of the traditional textile metrology any longer.

(Manuscript received May 15, 1953.)

Editor's note:

Dr. A. G. Scroggie, Chairman of the Definitions Subcommittee of the A.S.T.M. Committee D-13 on Textiles, assisted the editorial staff of TEXTILE RESEARCH JOURNAL in preparing the translation of Dr. Corbiére's paper for publication.

In comment, Dr. Scroggie offered his personal endorsement of the proposals made in the latter part of Dr. Corbiére's paper. He pointed out that they were a very worth-while and desirable extension of the more limited idea that "grex" and "tex" units are merely alternate terms in a single system, as stated previously (TEXTILE RESEARCH JOURNAL **19**, 292 (May 1949)).

Dr. Scroggie writes as follows: "Specific units will probably prove most convenient for typical textile structures, but where desired a single unit may be used for all structures if large numbers (and fractions) are not objectionable. In any case, the unit used must be designated, as we do with dollars and cents or pounds and shillings. The introduction of 'dex' and 'mex' units would make available additional terms which would be convenient for certain sized structures. It would appear that the ISO Committee on Textiles should consider the adoption of the proposed units and they might at the same time wish to designate the system as the ISO Yarn Numbering System."

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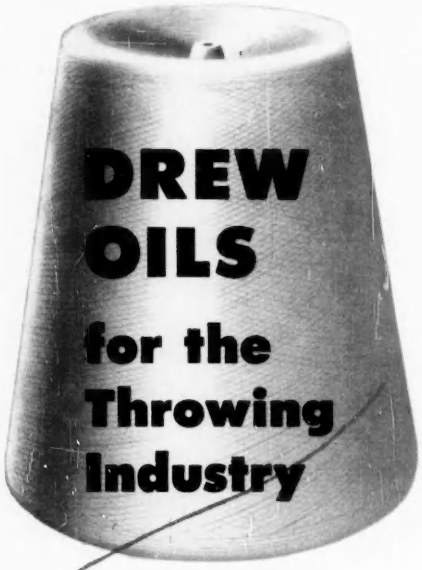

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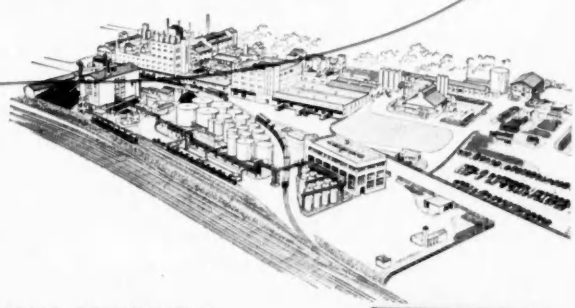

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